DRYING BUTANOL USING BIOSORBENTS IN A PRESSURE SWING ADSORPTION PROCESS

A Thesis submitted to the College of

Graduate Studies and Research

in Partial Fulfillment of the Requirements

for the Degree of Master of Science

in the Department of Chemical and Biological Engineering

University of Saskatchewan

Saskatoon

By

Divya Jayaprakash

PERMISSION TO USE

In presenting this thesis/dissertation in partial fulfillment of the requirements for a Postgraduate degree from the University of Saskatchewan, I agree that the Libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis/dissertation in any manner, in whole or in part, for scholarly purposes may be granted by the professor or professors who supervised my thesis/dissertation work or, in their absence, by the Head of the Department or the Dean of the College in which my thesis work was done. It is understood that any copying or publication or use of this thesis/dissertation or parts thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of Saskatchewan in any scholarly use which may be made of any material in my thesis/dissertation.

Requests for permission to copy or to make other uses of materials in this thesis/dissertation in whole or part should be addressed to:

Head of the Department of Chemical and Biological Engineering
57 Campus Drive
University of Saskatchewan
Saskatoon, Saskatchewan
Canada
S7N 5A9

ABSTRACT

A significant challenge in large scale industrial production of butanol is its low product titer. Butanol needs to be purified to higher than 99% purity in order to be used for fuel applications. The focus of this study is to selectively remove water from butanol-water vapor to achieve fuel grade butanol in a pressure swing adsorption (PSA) system using biosorbents developed from agricultural byproduct canola meal (CM). CM was characterized by Fourier Transform Infrared Spectroscopy (FTIR) that CM contains polar groups such as hydroxyls, carboxyls, and amines in cellulose, hemi-cellulose and protein that have the potential for water adsorption. Physico-chemical characterizations were also done to understand the major composition, elemental make-up, devolatilization characteristics and particle size distribution of the CM used.

The results demonstrated that biosorbent based on CM was able to successfully dry lower grade butanol and generate fuel grade butanol of over 99 v/v%. Five operating parameters were studied at two different levels to get the optimum process conditions for butanol drying, including temperature (95 and 111°C); pressure (135 and 201 kPa); feed butanol concentration (55 and 95 v/v %); feed flow rate (1.5 and 3 mL min-1) and particle size of adsorbent (0.425-1.18 mm and 4.7 mm pellets). Orthogonal array design (OAD) tool was used to design experiments and to evaluate the effects of these parameters. The performance of butanol dehydration was evaluated using five indices - water uptake; butanol uptake; water selectivity; butanol recovery; and maximum effluent butanol concentration in the effluent. The results demonstrated that feed butanol concentration, temperature and pressure were found to be the most significant factors overall, affecting most of the indices. The effects of individual operating

parameters on each butanol dehydration index were determined and a set of optimum operating conditions were proposed by the range analysis of the orthogonal array design at 111^{o}C, 135 kPa, feed butanol concentration of 55 v/v%, feed butanol-water liquid flowrate of 3 mL/min and biosorbent particle size of 0.43-1.18 mm. The experiments conducted at the above mentioned optimum conditions resulted in water uptake of 0.48 g/g-ads, water selectivity of 5.4, butanol recovery of 90%, and the maximum butanol concentration in the effluent being over 99 v/v% , which are better than that obtained at any other conditions investigated in this work. The Dubinin–Polanyi model based on adsorption potential theory displayed a goodness of fit to the water adsorption isotherm data with a r^2 value of 0.95 and average relative error of just 3.5%. The mean free energy determined from the model was 0.02 kJ/mol indicated the adsorption is physical. Thermodynamic parameters were also evaluated which revealed that the water adsorption is exothermic and spontaneous. Water saturated adsorbent was regenerated at 110°C under vacuum and reusability was studied.

The contribution of two major components of CM namely cellulose and protein were also examined for their capability to selectively remove water from butanol. The results showed both of them were able to dry water, however cellulose was found to have a higher water uptake and water selectivity than protein, indicating that it plays a major role in drying butanol.

In order to compare the performance of CM on drying of butanol with other biomaterials, adsorption experiments were done using corn meal as adsorbent, which is one of the most common starch based biosorbents for ethanol drying. The results demonstrated that canola meal had a higher water uptake and water selectivity than corn meal. Use of CM over corn meal adsorbent is also desirable so as to avoid placing pressure on food consumption. In addition, drying of butanol using other cellulose based biosorbents such as oat hull was also explored. Oat

hull demonstrated a potential to adsorb water and dehydrate butanol, which requires further in-depth investigation.

ACKNOWLEDGEMENTS

There are so many people than I can possibly name to thank for helping me through this journey. However, special thanks need to go out to people who have tremendously impacted me and my work.

First and foremost, I would like to express my genuine thanks to my supervisors, Dr. Catherine Hui Niu and Dr. Ajay Dalai for their guidance, constructive criticisms, suggestions, and support. I learned a lot from them. I thank them for their patience, unstinting support and encouragement!

My thanks also go to the members of my advisory committee for their many questions, guidance and suggestions:

Dr. Jaffar Soltan, Department of Chemical & Biological Engineering, University of Saskatchewan (Chair), and

Dr. Chithra Karunakaran, Beamline Scientist, Canadian Light Source Inc., University of Saskatchewan.

My heartfelt thanks go to my loving husband, Mohammed Zabiulla and my awesome Dad, Jayaprakash for their unconditional love and support, sacrifices, unending prayers, and encouragement through one of the most challenging things I have ever done. My Mother – Vijayalakshmi although isn't alive to celebrate this feat, I thank her for planting good seeds and thoughts in me. She dreamt of this day but never lived to see it come true, but I know that she is always with me. I felt her presence throughout the journey as a source of strength that kept me going. I thank her immensely! I am most grateful to God almighty for making everything possible – for giving me the opportunity to make a contribution to a research area about which I

am so passionate, for directing my path, especially in the choice of graduate school and supervisors to work with, and for giving me the strength I needed to complete my Master's program.

This thesis would not have been possible without the help and support of the members of the Chemical and Biological Engineering Department particularly Dr. Ravi Dhabhai, Mr. Richard Blondin, Mr. RLee Prokopishyn, and Ms. Heli Eunike. Thank you!

I'm also thankful to Bunge Global Innovation and Richardson Milling Ltd for their help with providing with biomaterials for research. Finally, I would like to thank the Saskatchewan Ministry of Agriculture, Saskatchewan Canola Development Commission, Saskatchewan Agriculture Development Fund, Western Grains Research Foundation, MITACS and Spectrum Technologies as well as University of Saskatchewan for their financial support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

Å	angstrom
C	water content at time t (wt%)
C_o	initial water content (wt%)
C_e	equilibrium water concentration in vapor phase (g/L)
E	mean free energy of adsorption (kJ/mol)
k_1, k_2	average values of the performance index for each of the parameters at levels 1 and 2 in OAD table (units of respective performance index)
K_1, K_2	pore constants for microspore and large pore materials (dimensionless)
K_o	equilibrium thermodynamic constant of the adsorption process (dimensionless)
P	pressure (atm)
P_i	partial pressure of the adsorbate (atm)
P^s	saturated vapor pressure of the adsorbate (atm)
q	mass adsorbed per unit mass of adsorbent (g/g-ads)
q_e	equilibrium water uptake (g/g-ads)
q_o	limiting mass for adsorption (g/g-ads)
R	universal gas constant (J/mol K)
r^2	correlation coefficient (dimensionless)
T	absolute temperature (K)
X_w	mole fraction of water in the adsorbed phase (dimensionless)
X_b	mole fraction of butanol in the adsorbed phase (dimensionless)
Y_w	mole fraction of water in the vapor phase (dimensionless)

Y_b	mole fraction of butanol in the vapor phase (dimensionless)
α	separation factor (dimensionless)
β	affinity coefficient (dimensionless)
ρ	fluid density (kg/m^3)
ε	adsorption potential (J/mol)
Δ	range value in statistical range analysis (units of the performance index)
$\Delta H°$	heat of adsorption (kJ/mol)
$\Delta G°$	Gibb's free energy (kJ/mol)
$\Delta S°$	entropy change (J/mol K)

ABBREVIATIONS

ABE	Acetone-Butanol-Ethanol
ARE	Average Relative Error
BET	Brunauer, Emmett-Teller
BSA	Bovine Serum Albumin
Bu-OH	Butanol
CM	Canola meal
CNPs	Carbon nanoparticles
FAO	Food and Agriculture Organization
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas chromatography
LLE	Liquid-Liquid Extraction
MT	Million Tonnes
OAD	Orthogonal array design
OH	Oat hull
PAH	Polycyclic aromatic hydrocarbons
PDMS	Polydimethylsiloxane
ppm	parts per million
PSA	Pressure Swing Adsorption
TG/DTA	Thermo gravimetric/Differential Thermal Analysis
TMT	Thousand metric tonnes
TSA	Thermal Swing Adsorption

USDA U.S. Department of Agriculture

1. INTRODUCTION

Diminishing supplies of crude oil coupled with environmental pressure to reduce greenhouse gas emissions and carbon footprints have led to a massive interest in renewable biofuels (Harper et al., 2009). Ethanol and butanol are the most common biofuels produced by fermentation (Shah and Dhrubo, 2011). In recent years, biobutanol is preferred to bioethanol and other alcohols, mainly because of its superior fuel properties that are very similar to gasoline. It is less corrosive and can be easily transported through existing pipelines. It also has higher volatility, combustion value, and octane rating with less ignition problems (Visioli et al., 2014). Above all, biobutanol can be used in place of gasoline without vehicle modifications – that means it can be integrated seamlessly into the existing petroleum infrastructure (Syntec Biofuel Inc., 2014). Butanol-gasoline blends of up to 85% butanol can be used in unmodified petrol engines (Nigam and Singh, 2011).

Biobutanol is often produced through acetone-butanol-ethanol (ABE) fermentation. However, as the main product, n-butanol is toxic to microorganisms above 2 wt% (2.45 v/v%) in fermentation broth (Moreira et al., 1981) and it is very difficult to obtain its high titer. Thus, it is imperative to purify butanol from diluted aqueous media. Unless concentrated to higher than 99 %, biofuels can neither be mixed with gasoline nor be used as a stand-alone fuel (University of California Television (UCTV) and Berkeley Lab, 2009).

Conventionally, for purification of butanol from ABE process, distillation is carried out to produce azeotropic vapor of about 55 v/v% butanol and 45 v/v% water followed by decantation and additional distillation. It is a costly and energy intensive process due to the need of a secondary or multiple distillation units for the decanted butanol (Kumar et al., 2013;

Melzoch et al., 2010). Distillation, followed by adsorption could be a cost-effective method in terms of energy requirement. A specific adsorption technique known as pressure swing adsorption (PSA) has been put to practice by most of the bioethanol industries due to its low energy requirement to achieve anhydrous ethanol (Simo, 2008; Tajallipour et al., 2013). Most commonly, zeolites are used as an adsorbents in PSA process owing to their high adsorption capacity. However, the regeneration of water saturated zeolite bed is energy intensive and their disposal can be a threat to environment. These shortcomings could be overcome with a more effective approach of using biomaterials as adsorbents as they are biodegradable, reusable (Sun et al., 2013); (Tajallipour et al., 2013), safe (Boonfung and Rattanaphanee, 2010), and doesn't pose a threat to be disposed of into the environment.

Agriculture byproduct like canola meal can be potential biosorbent, as canola (*Brassica juncea*) is abundantly cultivated in Canada (Agri-Food Canada, 2013; Newkirk, 2009). The byproduct has not been thoroughly investigated as adsorbent for drying biobutanol, although canola meal has been reported to have a relatively high water adsorption capacity of about 303-390% of its initial dry weight (Aider and Barbana, 2011). Research has demonstrated that canola meal, before (Baylak et al., 2012) and after (Ranjbar et al., 2013) protein extraction, is capable of drying ethanol, showing its potential for drying other alcohols. There is a great incentive in examining the low cost biomaterial for drying butanol. Therefore, in this work, a pressure swing adsorption process using canola meal based biosorbents was investigated to selectively remove water from lower grade butanol-water vapors including the simulated azeotropic butanol concentration (55 v/v%) from preliminary distillation in biobutanol production industry, to optimize the crucial parameters affecting the performance of drying butanol, and to explore the water selective adsorption mechanism. A novel aspect of this study was the approach of butanol

dehydration by selective water adsorption from the butanol-water vapor mixture on a biosorbent packed PSA column so that fuel grade butanol was produced directly from the effluent of the adsorption column. It was aimed to be an alternative to the use of multiple unit operations such as decantation and additional distillation units in the biobutanol production industry.

2. KNOWLEDGE GAPS AND OBJECTIVES

2.1 Knowledge Gap

Butanol has garnered active research interests and investments due to its superior fuel characteristics; yet the purification of butanol using adsorption technique like PSA hasn't been investigated. Despite being the most common method of ethanol purification in industries since 1980's, there is only limited information about the operation of PSA with biomaterials as adsorbents in it. Previous research demonstrated that canola meal (CM) successfully adsorbed water from ethanol-water mixtures when used as an adsorbent in PSA (Ranjbar et al., 2013; Tajallipour et al., 2013) showing a potential for drying other bio alcohols. Whereas the studies on the potential of biosorbent canola meal to dry water from butanol-water mixture was not reported. The mechanism of selective water removal from butanol-water mixture is not known. Therefore, there is an extensive incentive to investigate the capability of biomaterials as bioadsorbent in a PSA process to dehydrate butanol. This not only discovers new uses of the cost-effective material but will also enhance agricultural industry by selling their agricultural by-products to purify a promising alternative fuel biobutanol or the like.

Based on the discussion above, the knowledge gaps in the butanol dehydration process are as follows:

- Systematic characterization of CM for butanol dehydration has not been done yet.
- Investigation on adsorption capacity of CM has never been done for butanol dehydration.
- Determination of optimum operating conditions for butanol dehydration in a PSA have not been determined before.

- The water/butanol adsorption kinetics and equilibrium on CM for butanol dehydration have not been investigated.
- Study of contributions of major component fractions like cellulose and protein within CM have never been done yet.
- Regenerability and reusability of CM on butanol dehydration has never been examined.

2.2 Hypothesis

Literature review clearly shows that CM in its raw form or after protein extraction exhibited capabilities to dehydrate ethanol-water vapor. As alcohols share similar characteristic features in terms of polarity with respect to their hydroxyl functional group, CM may also dehydrate other commercially significant alcohols like butanol. Distillation followed by decantation to purify butanol is not just energy-intensive but also translates to a high operational cost due to the need for multiple distillation units. This drives the need to identify a cost-effective method along with the flexibility to use a variety of adsorbents, which makes adsorption a potential method following preliminary distillation for commercial butanol purification. Also systematical investigation on adsorption technique using any bio-material as adsorbents for butanol dehydration has not been reported yet. It is thus hypothesized that drying butanol-water vapor may be achieved successfully using CM based biosorbent in a pressure swing adsorption (PSA) system.

2.3 Research Objectives

The overall objective of this research is to determine the capability of CM for butanol dehydration in a pressure swing adsorption (PSA) process. Based on the knowledge gaps, the specific objectives are defined as follows:

1. Characterize CM biosorbent for butanol dehydration.
2. Determine the adsorption capacity of CM on butanol by the breakthrough curve technique.
3. Investigate the effect of operation parameters on butanol dehydration using CM in a pressure swing adsorption process
4. Determine and validate the optimum operating conditions for butanol dehydration generated by the orthogonal array design (OAD) method
5. Characterize the water adsorption equilibrium using Dubinin-Polanyi model
6. Determine the contributions of major components' in CM namely cellulose and protein to the selective water adsorption.
7. Investigate the regenerability, reusability and stability of CM

3. LITERATURE REVIEW

3.1 Butanol as fuels

The volatile crude-oil prices and issues of energy independence and carbon dioxide emissions have generated new interest in biofuels. Qureshi and Blaschek, (2006) discussed the advantages of n-butanol over ethanol as butanol's properties are similar to gasoline than ethanol: butanol has lower heat of vaporization, lower vapor pressure, higher octane number, and higher energy density (Qureshi and Blaschek, 2006). It is also less corrosive and can be easily transportable through existing pipelines, and non-hygroscopic and so less susceptible to water contamination (Luyben, 2008b).

Octane rating and energy density are the two important factors that determine an efficient biofuel. Table 3.1 shows that butanol comes closer to gasoline in these two measures, which reasons out why bio-butanol is favored over other alcohols and even the existing ethanol plants are getting retrofitted to produce butanol in commercial volumes (Syntec Biofuel Inc., 2014).

Table 3.1 Comparison of biofuels with gasoline (BioFuel.org.UK, 2014)

Fuels	Energy Density (MJ/L)	Average Octane (AKI Rating / RON)
Gasoline	~33	85-96 / 90-105
Butanol	~30	97/103
Methanol	~16	98.65/108.7
Ethanol	~20	99.5/108.6
Propanol	~24	108/118
AKI - Anti-Knock Index: This octane rating is used in Canada and United States		
RON-Research Octane Number: This octane rating is used in Australia and most of Europe		

For instance, Butamax Advanced Biofuel LLC, funded by DuPont Co. and BP Plc (BP/), is retrofitting an ethanol plant in Minnesota to produce butanol (Gismatullin and Lundgren, 2014).

3.2 Production processes of butanol – an overview

Butanol has been garnering much focus within the scientific and environmental community as a potential biofuel and apart from ABE fermentation, it can also be produced by few chemical and petrochemical routes. Some of the production methods of butanol are discussed below.

a) **Chemical processes**: Some of the following chemical methods are being used for manufacture of butanol.

In oxo-synthesis or hydroformylation, syngas reacts with propylene in the presence of metal catalysts like Co, Rh or Ru substituted hydrocarbonyls resulting in aldehyde-ketone mixture. Aldehyde alone undergoes hydrogenation to form butanol (Babu et al., 2013). High pressure process using Co produces 75% butanol while low pressure using Rh produces 92% butanol.

In a direct production process called Reppe synthesis, butanol is produced from a reaction involving propylene, carbon monoxide and water at low temperatures and pressures in the presence of a catalyst. A mixture of n-butaraldehyde and isobutaraldehyde are produced and the former is reduced to butanol (Babu et al., 2013).

Crotonaldehyde hydrogenation is an alternative route for butanol production from ethanol. Synthesis of butanol takes place through dehydrogenation of ethanol to acetaldehyde. The petrochemical process begins with propene that goes through a hydroformylation reaction and reduced with hydrogen to produce a mixture of approximately 88% butanol and 12% isobutanol.

Butanol is also produced from biomass such as agriculture or forest residues through the use of heat and catalysts termed as thermo-chemical process. This method refers to gasification,

combustion, fast pyrolysis, catalytic conversion or hydrothermal processing. This method suffers from major disadvantages like release of lots of dust and organic compounds in the exhaust apart from the high operating expense, biomass stock requirements and investments.

Butanol produced through petrochemical routes from fossil fuels is certainly not a sustainable option; especially in the distant future when large increase in butanol availability would be needed considering its use as motor fuels (Ladisch, 1991).

b) **Bio-chemical process - ABE Fermentation** - The major advantage of biofuels is that they can be generated from renewable biomass by use of engineered/ non-engineered micro-organisms in an anaerobic environment that lets them shut down their usual sugar metabolism but instead allow fermentation producing bio-alcohols. In butanol fermentation, also known as ABE fermentation or solvent fermentation, biobutanol is produced through anaerobic conversion of carbohydrates by strains of Clostridium species (*C. acetobutylicum* and *C. beijerinckii*) into acetone, butanol and ethanol (ABE) in the ratio of 3:6:1 as shown in Fig.3.1. It is one of the oldest industrial fermentations and largest biotechnological processes ever known (Chao et al., 2011).

The concentration of the main product, n-butanol (the most common butanol isomer produced in fermentation) produced in the fermenter is quite low because of toxicity problems as it exhibits product-inhibition when its concentration in the fermentation broth reaches 2 wt% (2.45 v/v%) (Babu et al., 2013; Moreira et al., 1981). Engineered bioprocess systems with genetically modified strains of *Clostridium* produced a relatively high titer butanol (Visioli et al., 2014) by manipulating the microbes to be more resistant to the effects of butanol. With engineered microbes in ABE fermentation, butanol concentration of about 20 g/L (2.45 v/v%) is produced (Ramey and Yang, 2004).

Thus, purification of low butanol titer to 99.7% butanol is thus essential in order to be able to use as biofuels or additives to gasoline (Lin et al., 2012b). Prominent companies like Dupont and BP Public Limited Company has made joint ventures in the name of Butamax Advanced Biofuel LLC to produce and market biobutanol (Gismatullin and Lundgren); other big players include Sovert (UK), Gevo, Cathay Industrial Biotech (China), Cobalt technologies, Green Biologics (UK), Butyl Fuel LLC (US), Butalco (Switzerland), Gourmet Butanol (USA) are also involved in biobutanol production (Chao et al., 2011).

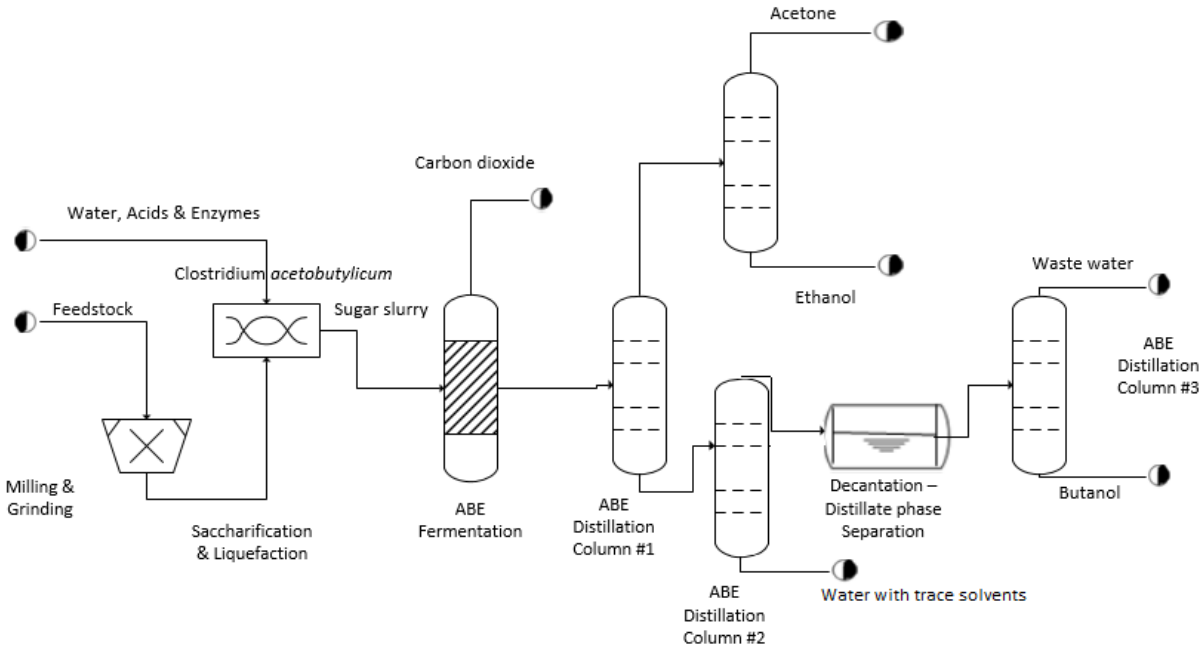


Figure 3.1 Butanol Production by ABE fermentation (Kumar et al., 2013)

Most butanol in US has been manufactured from petroleum and other fossil fuels using petro-chemical processes since 1950's because the price of petrochemicals dropped below that of starch and sugar substrates such as corn and molasses (Chao et al., 2011).Therefore, butanol production from fossil fuel became more popular. In the 1970s, the oil crisis paved way to the

development of biofuels. At that time, the primary focus for alternative fuels was on ethanol. For the past 45 years, the energy-intensive ethanol process still has not solved our fuel, power or clean air requirements and so many countries are retrofitting bioethanol plants to produce biobutanol.

In an attempt to solve our fuel and clean air requirements and in response to the rising pollution and complement the use of petrochemicals, industries are reexamining fermentation as a source of butanol in many countries (Chao et al., 2011).

3.3 Conventional methods of purification of bio-butanol

The conventional industrial approach for purification of biobutanol generated from ABE process is distillation of butanol from fermentation strength to 55 v/v% butanol followed by dehydration technique like decantation to remove the remaining water. In general, the butanol is separated from the fermentation broth containing organic matter, sugars, solvents and other impurities during distillation while the water is removed from butanol in the dehydration process. Other techniques for purification of butanol include the liquid-liquid extraction, membrane separation, gas stripping and adsorption and are briefed below.

3.3.1 Distillation and Decantation

Distillation followed by decantation is the final separation step used to separate and purify butanol from the ABE fermentation broth (Melzoch et al., 2010). Butanol being a lipophilic solvent is less soluble in fermentation broth and forms a distinct phase from the other solvents produced (Babu et al., 2013). The butanol is distilled from the fermentation broth containing acetone, ethanol, organic matter and other impurities. The overhead product of

secondary distillation unit is partially pure butanol (55 v/v%) that is allowed to phase separate by decantation into butanol and water rich phases (Kumar et al., 2013). The decanted butanol rich phase will still have some water in it as the water solubility in n-butanol is 20.6 wt% (BASF, 2008) and is fed into a tertiary distillation unit to achieve high pure butanol (Kumar et al., 2013). As butanol has low vapor pressure and high boiling point (118°C), multi-step distillation is extremely energy intensive.

Separation scheme of distillation followed by decantation has some serious issues such as requirement of high energy and operating costs due to the need for multiple distillation units.

3.3.2 Liquid-Liquid Extraction (LLE)

It works based on the difference in the distribution coefficients (or solubility) of solvents in the extractant (usually oleyl alcohol and n-decanol) and aqueous phase for separation. Since butanol is more soluble in organic phase (extractant) than aqueous phase (fermentation broth); it is selectively concentrated in extractant (Babu et al., 2013).

The disadvantage with this method is the emulsion formation and toxicity of extractant to cells.

3.3.3 Membrane separation

Membranes are used within the ABE fermentation system for continual withdrawal of product butanol and to increase bacterial tolerance and productivity. Perstraction and pervaporation are two major methods**.**

Perstraction is a form of membrane extraction method or better known as LLE in presence of membrane that uses an extractive solvent on one side of membrane system and

fermentation broth flows past the membrane due to butanol's affinity for the solvent (Ramaswamy et al., 2013).

Pervaporation is a method in which fermentation broth is passed through a membrane with vacuum imposed on other side. Volatile components flow past the membrane and get vaporized by the low pressure on the vacuum side of the membrane and the product is then condensed and collected out. Membranes that are used for this process includes a blend of polyacrylonitrile and polyvinyl pyrrolidone, PDMS and cross-linked styrene-butadiene membrane (Kumar et al., 2010; Namboodiri and Vane, 2007; Ramaswamy et al., 2013).

Some of its demerits are high capital and operating costs, fouling, concerns on chemical resistance and longevity of membranes and the actual process being slow.

3.3.4 Gas stripping

This can either be integrated with ABE fermentation system or done separately and accordingly uses either nitrogen or fermentation gases (H_2 and CO_2) for stripping (Ramaswamy et al., 2013). In either case, the volatile solvent in the fermentation broth is captured by the stripping gas. In in-situ recovery, the gas containing solvents is condensed and enriched condensate is collected out while in the separate stripper method, the feed that is low in solvents is recycled back to bioreactor (Kumar et al., 2013).

Challenges such as low selectivity and high processing costs still exist in this method.

3.3.5 Adsorption

It is a surface-based phenomenon wherein the adsorbate forms a thin layer on the adsorbent after diffusing through it and gets desorbed or regenerated. High separation factor and

adsorption capacity are the two important criteria for screening the adsorbents (Ramaswamy et al., 2013). Application of adsorption for butanol purification has two possible approaches: selective butanol adsorption and selective water adsorption. In the adsorption process where butanol gets adsorbed onto adsorbents, product recovery is possible only during regeneration or desorption. As water molecules are also found to be adsorbed during this process along with butanol, a sequential heating desorption is preferred to obtain a concentrated butanol solution as a final product (Qureshi et al., 2005). Other potential problems with this approach could be the incomplete butanol recovery (Qureshi et al., 2005), need for an external agent like methanol for desorption (Yang et al., 1994), structural damage and change in stability of adsorbents after a sequential heat treatment. Factors like rate of adsorption and desorption and also ease of desorption play a major role in butanol recovery. In the adsorption process where water gets selectively adsorbed (often called dehydration), concentrated butanol is obtained as a direct final product from the effluent of the adsorption columns, and regeneration of the saturated columns were done thereafter. There are a few, but not sufficient research has been done on using this approach for butanol. For example, there is only one done by Westgate and Ladisch (1993) for vapor phase water adsorption from butanol, but the work was preliminary. However, a similar approach was successfully used to dry ethanol, and regenerate the column at a temperature no higher than 110^{o}C (Ranjbar et al., 2013; Tajallipour et al., 2013).

3.4 Dehydration using adsorption

3.4.1 Adsorbents

For any adsorbent material to be efficient and operative in an adsorption system, it is desired to possess a large internal surface area attainable to the species being separated from the

bulk phase (Anozie et al., 2010). Furthermore, it should indicate good mechanical and kinetic properties. The former associates with resistance to attrition and strength, while the latter means being able to convey the adsorbate to the adsorption sites (Thomas and Crittenden, 1998). In addition, it has high water uptake and selectivity, and reusability.

3.4.1.1 Inorganic adsorbents

In the approach of butanol purification by selective adsorption of butanol over water, mostly used adsorbents are synthetic zeolites (silicalites), molecular sieves and activated carbon (Ramaswamy et al., 2013), and uses of grafted polymeric-calixarenes were also reported (Thompson et al., 2011).

Qureshi et al., (2005) reported the recovery of butanol by adsorption using silicalites (85-97 mg/g), polymeric amberlite resins such as XAD-2 (78 mg/g), XAD-4 (100 mg/g), XAD-7(69 mg/g) and XAD-8 (66 mg/g), bone charcoal (206 mg/g), activated charcoal (130 mg/g), bonopore (74 mg/g) and polyvinylpyridine (68 mg/g). They concluded that use of silicalite is more attractive amongst the rest experimented as it was able to concentrate butanol from dilute solutions (5 to 790 g/L) with complete desorption of butanol (Qureshi et al., 2005). For regeneration of all these inorganic adsorbents, a stream of carrier gas at 190 °C- 288 °C is required (Beery and Ladisch, 2001). High regeneration temperature and disposal of synthetic inorganic adsorbents which is a threat to environment are the significant problems with the usage of inorganic adsorbents.

3.4.1.2 Biosorbents

Although no systematic research works have been done or reported with biosorbents for butanol dehydration, innumerous studies reported use of biomaterials as adsorbents for selective

adsorption of water from ethanol water mixtures. In this approach, biomaterial adsorbents can be divided into two groups: cellulosic and starchy materials.

Cellulosic materials: Wheat straw, barley straw and wood chips are some of the important cellulosic biosorbents and their sorption capability are attributed to their xylan, cellulose and hemicellulose content.

Researches have been done on water uptake by natural and activated palm stone, natural corncobs and oak by analyzed Al-Asheh et al., (2004) that showed that only activated palm stone has the highest water uptake capacity (0.09-0.19 g/ g dw bio sorbent) than the other biosorbents analyzed.

Benson and George, (2005) used a slightly different approach called thermal swing adsorption to evaluate the adsorption efficiencies of 3 lignocellulose based biosorbents for selective water adsorption and their recommendation based on water adsorption capacity in the order are: bleached wood pulp, kenaf core and oak sawdust.

Water adsorption capacity in a liquid ethanol-water system was comparatively observed on the following biomaterials- barley straw, wheat straw and crab shells (*Ucides cordatus*) by Sun et al., (2007). They confirmed that the barley straw showed highest water uptake (0.43± 0.01 mol/g dry bio sorbent) followed by wheat straw (0.22 ± 0.02 mol/g dry biosorbent) and then the acid washed crab shells (0.019 ± 0.001 mol/ g dry bio sorbent) (Sun et al., 2007).

Work on canola meal before (Baylak et al., 2012; Tajallipour et al., 2013) and after (Ranjbar et al., 2013) protein extraction show the capability of the meal to dehydrate lower grade ethanol to fuel quality one.

The ability of cellulosic components to selectively adsorb water is a result of interaction in the form of hydrogen bonding between free hydroxyl groups (-OH) on their glucose units and

the water molecules (Boonfung and Rattanaphanee, 2010) and alternatively by capillary action (Sun et al., 2013)

Starchy materials: Adsorption capacities of starch (corn and potato), and corn residue were analyzed and found that the high concentration of amylopectin in starch and corn residues attributed to their water adsorption capacities (Ladisch et al., 1984). Another comparative study was done on cassava starch pearls and corn grits by Youngmi et al. (Youngmi et al., 2011) which concluded that corn grits have lower equilibrium adsorption capacities than cassava pearls which is due to their smaller surface area.

Adsorption capacities of starch (corn and potato), xylan, pure cellulose and corn residue were analyzed and found that the high concentration of amylopectin in starch and corn residues attributed to their adsorption capacities (Ladisch et al., 1984) and based on it, were arranged in the decreasing order: corn starch, corn residue, xylan and pure cellulose (Kumar et al., 2010).The starchy materials usually have high water uptake than cellulosic materials (Kumar et al., 2010), however, use of them in alcohol drying industry places a pressure of food consumption.

3.4.1.2.1 Canola meal and other potential biosorbents

Canola being one of the most valuable oilseed crops in Canada with a $19.3 billion (as of 2013) contribution to Canada's economy is grown extensively in the province of Saskatchewan for well over 30 years (Canola Council of Canada, 2014). Statistics Canada has reported a 29.5% increase in production of Canola nationally to a record number of 18 MT in 2013 accounting from an average yield of 40 bushels per acre. Saskatchewan being the leading province in Canola cultivation alone has a production contribution of 8.9 million tons (Statistics Canada, 2014a).

Canola meal is one of the byproducts of canola industries including oil extraction and biodiesel production.

After the oil extraction (44%) from canola seeds, canola meal which is the protein-rich residues (36%) is used in the production of protein (Aider and Barbana, 2011; Newkirk, 2009). This protein meal is a routine source of energy to animals, poultry and even aquaculture feeds due to its high concentration of digestible amino acids (Newkirk, 2009). Canola meal on a moisture basis (12%) has 20% neutral detergent fiber comprising cellulose, hemicelluloses and lignin, 5% starch and 10% free sugar and non-starch polysaccharides (Canola Council of Canada, 2014).

The cellulosic components remained in the meal were considered to be responsible for water adsorption due to electrostatic forces between hydroxyl groups of the biosorbent and water molecules (Ranjbar et al., 2013). Considering its enriched composition of well-balanced and easily digestible amino-acids, its common use as animal and poultry feeds and also due to a long debated topic of Food vs. Fuel, it becomes important not to thrust any force on the food industry nor its consumers. The decision to utilize the canola meal after protein-extraction is thus appropriate.

Corn meal: Corn is the most produced cereal crop worldwide and it outstrips both rice and wheat in terms of global production. According to Food and Agriculture Organization (FAO), corn is the number one cereal crop worldwide with 885.3 MT produced in 2011 (USDA, 2015). Corn for grain is the third largest grain crop in Canada and the production of corn meal from the mills is also on the rise due to increased production. Corn meal by definition is the dried and ground corn kernels. In a typical yellow corn kernel on a moisture basis, starch forms 72 to 73 of its proportion followed by protein and plant fibre each forming 8 to 14 of its proportion

(Hamel and Dorff, 2015). On a dry basis, corn meal has 8% crude protein and is an important source of nutrition. Corn meal was found to be of particular interest as it was demonstrated to be capable of yielding anhydrous ethanol from lower grade ethanol due to its starch content (Beery and Ladisch, 2001; Hong et al., 1982; Ladisch and Dyck, 1979; Ladisch et al., 1979; Ladisch et al., 1984). Despite showing strong potential for water adsorption, literature doesn't provide information about its capability to dry butanol. Hence examining its water adsorption capacity from butanol-water mixture is of considerable interest in this work.

Oat hulls: Canada is the second leading oat producer in the world and U.S. Dept. of Agriculture has reported an annual production of 2,680 TMT of oats in Canada (USDA, 2014). There has been an increase in the oat milling by-products due to increased cultivation of oats and growth of oat-milling industries. Oat hulls make up 25% of the total oat and are characterized by high fibre content (Thompson et al., 2002). Due to presence of lignin in oat hulls, it has a very poor digestibility unlike canola meal. Oat hulls have 6.8% moisture, 7.28% protein, 3.6% ash, 26.8% acid detergent fibre, 19.8% crude fibre, 2.9% fat and 33.9% starch in them. Its chemical composition limits its nutritive value to that of low-quality forage and it has only been used as an adsorbent for heavy metal recovery like arsenic so far (Crini and Badot, 2010). Its high amount of starch shows the potential to dehydrate alcohols.

Use of these low-cost biomaterials as biosorbents could add value to agricultural waste products and thus the benefits might certainly be perceived by both the fuel and agriculture industries.

3.4.2 Pressure Swing adsorption (PSA) technique

PSA basically implies the adsorption and desorption methods done by swinging the parameter- pressure (Japan EnviroChemicals, 2014). This technology usually deploys some adsorptive materials like zeolites, molecular sieves and activated carbon that helps separate out a target gas species from a mixture of gases by way of adsorption under varying pressure. Though no results reported for butanol dehydration in a PSA process, uses of biomaterials as adsorbents for ethanol dehydration were reported (Baylak et al., 2012; Ranjbar et al., 2013; Tajallipour et al., 2013).

At moderate or high pressure, the target species are adsorbed on the surface of adsorbents and at low pressure they get released or desorbed. Swinging between pressures as in PSA is far more feasible than swinging between high and low temperatures as in a Thermal Swing Adsorption (TSA) as it takes longer time to exchange thermal energy (Japan EnviroChemicals, 2014).

As available in the literature there have been many research done on ethanol dehydration with PSA system using cassava (Boonfung and Rattanaphanee, 2010), canola meal (Baylak et al., 2012; Tajallipour et al., 2013), protein-extracted canola meal (Ranjbar et al., 2013), 3A zeolites (Rivera et al., 2013) and a two- or three bed PSA is the preferred and established method for the separation of water-ethanol mixtures for ethanol production (Ramaswamy et al., 2013). It's determined that adsorption kinetics and equilibrium both affect the PSA process.

3.5 Adsorption kinetics

Dynamics of adsorption can be studied by way of breakthrough curves; the plots of relative water concentration (C/C_0) vs. time termed as water breakthrough curve and the plot of

alcohol concentration (v/v%) vs. time is called alcohols breakthrough curve. There are no kinetics study reported for butanol dehydration using biosorbents, however, there are for ethanol. In the cases of ethanol dehydration, the samples are collected during adsorption at fixed time intervals and the time period when the fuel grade alcohols is obtained indicates the breakthrough time which also corresponds to 1 wt% of water (Tajallipour et al., 2013). Breakthrough curves were used to determine water/ethanol uptake through mass balance of the respective components in feed and effluent at breakthrough and saturation. The breakthrough point helps to compare and evaluate the adsorption performance of the bed under various operating conditions discussed before. As alcohols could also get adsorbed along with water, it is necessary to find water adsorption selectivity over alcohol which is given by a separation factor α (Baylak et al., 2012). Separation factor or selectivity of adsorption can be found by ratio of mole fraction of water to butanol in the adsorbed phase to that of mole fraction of water to butanol in the vapor phase. Water or butanol uptake can be determined by the mass balance calculations i.e. from the water/butanol input minus the water/butanol output per unit dry mass (g) of adsorbent in the column. Recovery of butanol is calculated at the end of adsorption process by the ratio of amount of butanol in the output to that in the input.

In the adsorption process, overall mass transfer resistance driving the uptake of adsorbate is divided into at least 2 resistances: 1) external film resistance- resistance in the fluid phase surrounding adsorbent particles, 2) macropore/micropore resistance- transfer of adsorbate molecules from the surface of the adsorbent to adsorbent particle pores (Bobok and Besedova, 2003). Rate controlling step for adsorption is usually determined by the mass transfer of adsorbate molecules on to the adsorbent. Kupiec et al. (2003) had concluded that in the isothermal adsorption of ethanol-water system, micropore diffusion was the rate – controlling

mechanism (Ranjbar et al., 2013). Rate controlling step could also be influenced by the experimental conditions and varying operational parameters such as flow rate, temperature, particle size, and feed concentration (Satterfield, 1980). Tajallipour et al., (2013) used a mass transfer model describing the breakthrough curve of water using canola meal as adsorbents in ethanol dehydration.

3.6 Adsorption Equilibrium

When adsorption rate equals desorption rate, state of equilibrium is attained and that equilibrium relationship is described by adsorption isotherms. The adsorption isotherm relates the amount of substance adsorbed onto the adsorbent at equilibrium to the concentration of the adsorptive species in fluid or pressure at a given temperature (Satterfield, 1980).Various isotherm models exist for predicting this equilibrium distribution and commonly used models include Langmuir, Freundlich, Temkin, Brunauer, Emmett-Teller (BET), potential theory models, etc.

Langmuir model was found to fit the water isotherm in ethanol dehydration by 3A zeolites in a PSA (Rivera et al., 2013). Adsorption isotherm study was carried out on Freundlich, Temkin and Langmuir models but only Langmuir was found to have the best fit of all in ethanol dehydration by starch adsorbents (Okewale et al., 2013). BET isotherm represented the adsorption data of ethanol vapor on starch (Lee et al., 1991). A hybrid isotherm featuring both Langmuir and Freundlich isotherms, are also available in case of Redlich-Peterson and Sips and Toth isotherm models (Shahbeig et al., 2013).

Apart from these regular fundamental isotherm models, there are also various other models developed to elucidate and investigate the mechanism of adsorption in an adsorption system. For instance, the models based on adsorption potential theory have attracted interests due to its reasonable revelation of physical meaning from the model parameters. Dubinin-Radushkevich model was initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism. It's used to distinguish the physical & chemical sorption of metal ions and is an improved model based on adsorption potential theory (Okewale et al., 2013). Another multilayer adsorption model derived from the potential theory is Frenkel–Halsey–Hill. Hill model assumes that adsorption is a cooperative phenomenon, i.e. the ligand binding ability at one site on the macromolecule, may influence different binding sites on the same macromolecule. The above discussed potential theory models solely apply to either micropore or macropore molecules. Among these models, Dubinin-Polanyi model based on potential theory has been used to represent the gas-solid equilibrium data for both micro and macropore molecules. A similar kind of modelling approach was done on water adsorption equilibrium on carbon nanomaterials (Yang et al., 2006), corn meal (Chang et al., 2006b), modified rice husk (Dada et al., 2012) and canola meal (Ranjbar et al., 2013). It has been recognized as the most powerful available theory for dealing with both gas and aqueous adsorption on energetically heterogeneous surfaces such as biomass.

4. MATERIALS AND METHODS

4.1 Biosorbent preparation

Protein extracted canola meal (CM) was obtained from Bunge Global Innovation, White Plains, NY, USA, while oat hull residues (OH) were obtained from Richardson Millings Ltd, Warman, SK, Canada. Both biomaterials were oven dried for 24 h at 105°C followed by sieving using Canadian Standard Sieves Series (Combustion Engineering Canada Inc.) to segregate particles of <0.43 mm, 0.43-1.18 mm and >1.18mm. Biosorbents with the particle size of 0.43-1.18 mm were used for the experiments based on the surface area and ease of operation in the column. CM were made using a California Pellet Mill (CPM-Laboratory Model CL-5, California Pellet Mill Co., Crawfordsville, IN, USA). The size of the pellets was about 4.7 mm in diameter and 7-10 mm in length. Cellulose (C-6288) and protein (S-9633) in the size range of 0.03-0.15 mm and 0.03-0.19 mm respectively were obtained from Sigma Aldrich and were used as such without any pretreatment as they were dry enough. Corn meal manufactured and supplied by Purity Inc, a trademark company of ADM Agri-Food Industry Ltd was used. Corn meal in the size range of 0.4- 1.13 mm was dried for 6h at 105°C to remove any residual moisture and was then used.

4.2 Feed solution preparation

Butanol solutions of different concentrations were prepared by mixing butanol (Fisher Scientific, ACS reagent grade; >99.4%) with distilled water.

4.3 Physico-chemical characterization of biosorbents

The major composition of CM was determined by Intertek Labs, Saskatoon, Canada as per AOAC International. The organic elemental content was analyzed using an Elementar Vario III CHNS analyzer. 4-6 mg of sample was weighed and packed along with a tin boat and placed in the designated chambers for analysis. Sulfalinic acid ($C_6H_7NO_3S$) was used as a standard for analysis. Fourier transform infrared (FTIR) spectroscopy (Bruker Vertex 70 FTIR spectrometer, MA, USA) analysis was carried out to identify the significant functional groups in biomass with respect to adsorption. Each spectrum was the average of 16 co-addition of scans with a total scan time of 15 s in the IR range of 400–4000 cm^{-1} at 4 cm^{-1} resolution. The devolatilization characteristics of the biomass with temperature was investigated by thermogravimetric analysis (TGA) (PerkinElmer Pyris Diamond TG/DTA) in the range of 22°C to 400°C at the rate of 5 °C/min. Particle size of CM was measured using Mastersizer MS-64 sample dispersion analyzer by means of dry method. A 1000F lens was utilized and the particle size analysis was performed using 10,000 sweeps, and the obtained particle obscuration was comprehended between 10% and 30%.

4.5 Adsorption / desorption experiments

The PSA system used in this study has been used previously for ethanol drying (Ranjbar et al., 2013; Tajallipour et al., 2013) and the schematic drawing is presented in Fig. 4.1. The system consists of a stainless steel fixed bed column with dimensions of 500 mm long (inside), 47.50 mm ID, and 1.65 mm wall thickness. There is an oil heating jacket that is used to maintain constant temperature of the column throughout the adsorption process. In order to simulate the

butanol-water vapor generated by preliminary distillation in biobutanol production industry, butanol-water liquid solution stored in a sealed jacketed feed tank was pre-heated to 90°C and passed through a pump (Cole- Parmer, RK-74930-05) to stainless steel tubing equipped with heating tapes (Cole-Parmer; 50-60Hz, 120 V, 624W, 5.20A) to vaporize in which they were mixed with nitrogen gas (carrier gas) at a flow rate of 850 mL min^{-1}. Complete vaporization of the feed butanol solution before feeding to the adsorption column was ensured. This is also to avoid liquid water entering the column to cause organic carbon leaching from biosorbents which may produce colored effluents and thus reduce the product quality. The vapor feed entered the column from the top through a three-way valve. The adsorption experiments were carried out based on the principle of PSA i.e. by swinging between pressures as shown in the experimental set-up sin Fig 4.1. Temperature is controlled and read at the top and bottom of the column by two thermocouples (Omega K type, US) which are attached to Omega DPI32 outputs. The pressure was measured at top and bottom of the column and pressure drop along the column during the adsorption process was 2.1-3.2 kPa, which is negligible. A back pressure regulator is used to maintain isobaric operation during the adsorption process. The pressure of the column at the bottom is controlled by a pressure transducer (Honeywell, US) attached to a DPIS32 output. Water got selectively adsorbed onto the bed and the dried butanol product stream exited from the bottom of the column. The effluent was then condensed and collected for water content analysis by a KF titrator. The sample was collected at an interval of 5 min and the adsorption process lasted for a total duration of about 2.5 h till equilibrium (bed saturation) was achieved. The bed is considered saturated when the temperatures at the top and bottom of the bed reached the inlet temperature of the vapor.

After adsorption, regeneration of column was carried out by purging nitrogen gas (flow rate 850 mL min^{-1}) from the bottom of the column and applying vacuum of about 33 kPa at 110°C for 5.5 h which was confirmed sufficient to dry the wet column.

Water or butanol uptake was determined by the mass balance, i.e. the water/butanol input minus the water/butanol output per g of adsorbent in the column. Recovery of butanol was defined as the ratio of the amount of butanol in effluent to the amount of butanol in influent. Water separation factor or selectivity of water adsorption (α) was estimated as:

$$\alpha = (X_w/X_b) / (Y_w/Y_b) \quad (4.1)$$

where X_w is mole fraction of water in the adsorbed phase, X_b is the mole fraction of butanol in the adsorbed phase, Y_w is the mole fraction of water in the vapor phase and Y_b is the mole fraction of butanol in the vapor phase.

The water content was determined by an automated Karl-Fischer coulometric titrator (Mettler Toledo DL 32) using methanol for dilution as the titrator is sensitive to water content lower than 5 wt%. Butanol content in the effluent samples was calculated by the total mass of sample minus water mass, which was also cross validated with that measured by a gas chromatograph (GC) (Agilent Technologies 7890A GC System; 7683B Series Injector) with a flow ionization detector. Butanol analysis was carried out at the following conditions - flow rate 2.6 mL min^{-1}, average velocity 40 cm sec^{-1}, hold up time 1.25 min, inlet temperature 150°C, oven temperature 40°C and detector temperature 250°C. 25 µL sample was injected into the column with a split ratio of 100:1.

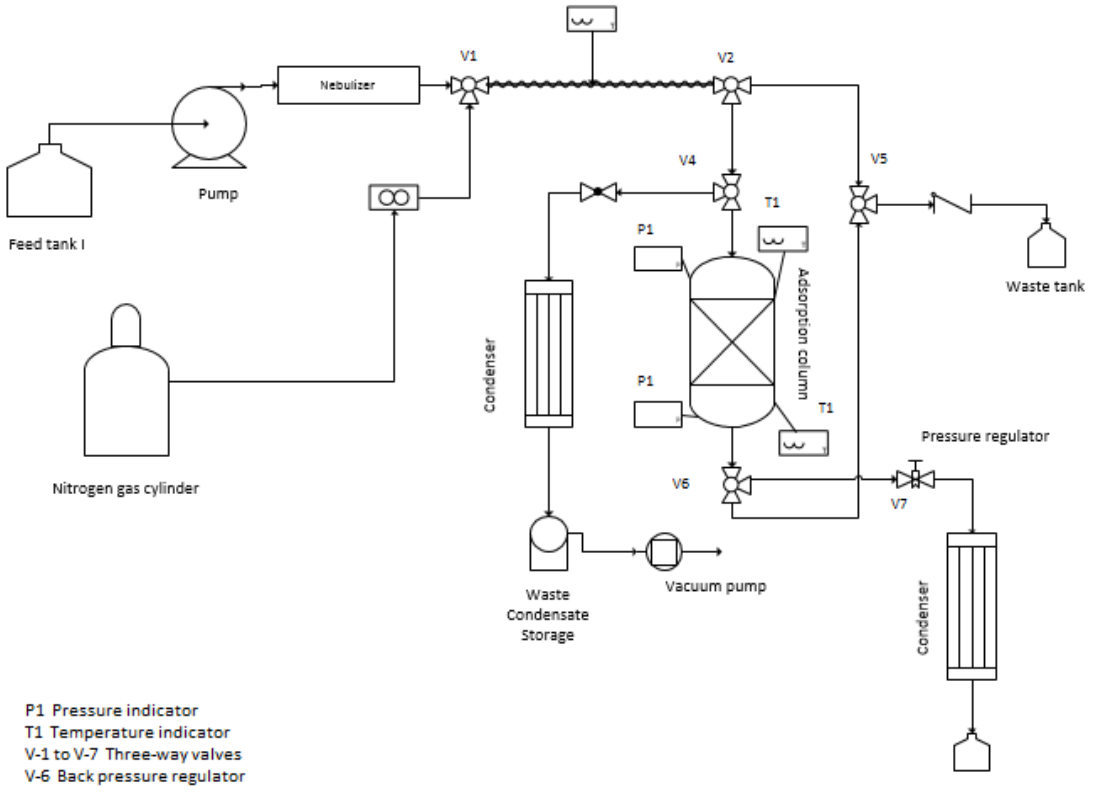


Figure 4.1 Schematic diagram of the experimental PSA setup

4.4 Design of experiments by Orthogonal Array Design (OAD) tool

In order to evaluate the effects of operating parameters on butanol drying, orthogonal array design (OAD) was used. Five operating parameters including temperature (A), pressure (B), butanol feed concentration (C), feed flow rate (D), and size of adsorbent particles (E) were chosen for the present study as shown in Table 4.1. The number of experiments were determined to be 8 according to OAD for 5 parameters considered at two levels (Medina et al., 2009). The levels 1 and 2 for temperature; pressure; butanol feed concentration; feed flow rate; and particle sizes were chosen at 95 and 111°C; 135 and 201 kPa; 55 v/v% and 95 v/v% ; 1.5 and 3 mL min^{-1}; and 0.425-1.18 mm and 4.7 mm, respectively. The butanol feed concentrations of 55 and 95

v/v% were chosen to mimic the azeotropic distillate butanol concentration and the high end of concentration, and the corresponding boiling points (95 and 111°C) were chosen to study the effect of operation temperature. A pressure range of 135-201 kPa was chosen to avoid high pressure operation demanding high energy consumption. The effect of these parameters on performance indices, including water uptake, butanol uptake, water selectivity, butanol recovery, and maximum effluent butanol concentration were determined using a statistical treatment called the "range analysis" (Sharma et al., 2005). This is to provide with relevant information to optimize the butanol dehydration performance by choosing appropriate operation conditions. All the experiments were replicated and the average results with standard deviation were reported.

Table 4.1 Factors and levels in orthogonal array design experiments

	Factors				
	A	**B**	**C**	**D**	**E**
Levels	Temperature (°C)	Pressure (kPa)	Bu-OH Feed Concentration (v/v %)	Feed flow rate (mL min^{-1})	Particle sizes (mm)
L 1	95	135	55	1.5	0.425-1.18
L 2	111	201	95	3.0	4.7

5 RESULTS AND DISCUSSION

5.1 Physico-chemical characterization of CM

Composition: The major composition of CM is presented in Table 5.1. CM was found to contain over 26% cellulose and lignin, and 6.3% hemicellulose. The high content of cellulosic components is desirable in biomass as these groups are responsible for water adsorption (Ranjbar et al., 2013). Even after protein extraction, the residual protein of CM was found to be around 27%. The efficiency of protein extraction from CM in the industry is out of the scope of this work.

Table 5.1 Composition of canola meal

Content in CM	Composition (wt%)
Protein	27.1±0.53
Starch	< 1.5
Acid detergent fibre (Cellulose +Lignin)	26.4±0.42
Hemicellulose (%)	6.3±0.56
Ash	3.6±0.17
Moisture	4.2±0.9

Elements: The major organic elements of fresh CM are presented in Table 5.2. CM primarily contained carbon which is due to the presence of protein, cellulose, hemicellulose, and lignin. It also had higher nitrogen content due to residual protein. The cellulose owns a crystalline structure made up of microfibrils that are linked together by hydrogen bonding and

are enclosed by amorphous hemicelluloses. The lignin is instrumental in keeping the other components together.

Table 5.2 Organic elemental composition of fresh and used canola meal (in wt%)

Element	Fresh (unused) CM	CM after adsorption and regeneration
C	46.34±0.04	46.85±0.13
H	6.15±0.03	6.60±0.04
N	3.78±0.08	3.85±0.07
S	0.35±0.06	0.33±0.01

FTIR: In order to determine the presence of various functional groups present in CM, FTIR spectrum was obtained as shown in Fig. 5.1. The spectrum showed that most intense peak obtained at 1100-1000 cm^{-1} indicates C-O group owing to the presence of polysaccharides (Himmelsbach et al., 2002) such as cellulose, and hemicellulose. The C–N stretching vibration of aliphatic amines is observed as medium or weak bands in the region of 1250-1020 cm^{-1} which is indicative of presence of amino acid groups in residual protein (Theivandran et al., 2015). It is known that appreciable amounts of glucomannan and xylan are part of hemicellulose. Thus the presence of C=O band at 1730 cm^{-1} along with C-H asymmetric and symmetric stretching vibrations at 2950 cm^{-1} provide information about presence of hemicellulose (Himmelsbach et al., 2002). A prominent peak at 1700 cm^{-1} is due to C=O stretching attributed to lignin in biomass. The asymmetric stretching vibration observed at 1650 cm^{-1} is most likely due to the presence of amines. In the spectrum, the broad peak at 3300–3450 cm^{-1} is attributed to -OH stretching (Kumar et al., 2009).

The affinity of water towards biomaterials is basically due to the presence of polar groups such as hydroxyl and carboxyl functional groups. For instance, hydroxyl groups on

cellulose/hemicellulose in a cellulose-based adsorbent (Okewale et al., 2013) and on amylopectin in starch-based adsorbents (Beery and Ladisch, 2001) are responsible for adsorption of water by forming hydrogen bond between the hydroxyl groups on the surface of the adsorbents and the water molecules (Boonfung and Rattanaphanee, 2010).

The FTIR spectrum of CM shows CM contains polar groups such as hydroxyls, carboxyls, and amines in cellulose, hemi-cellulose and protein that have the potential for water adsorption.

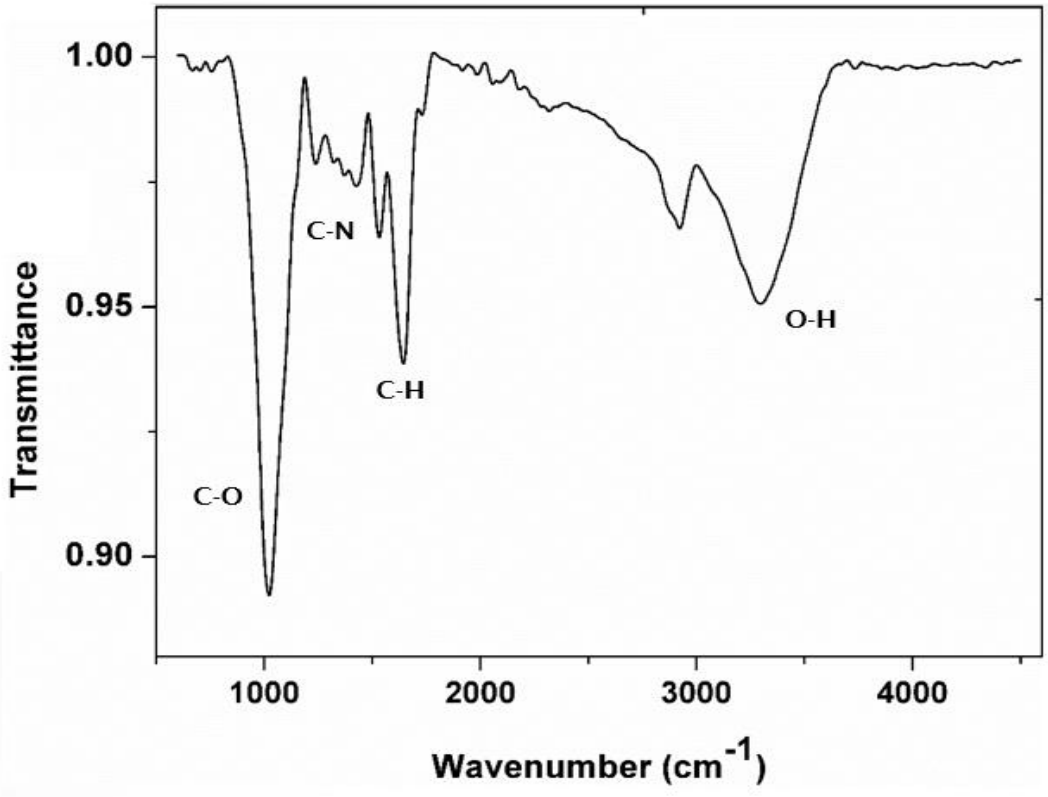


Figure 5.1 FTIR spectra of canola meal

TGA: The devolatilization characteristics of canola meal obtained from TG/DTA analysis is depicted in Fig. 5.2. As it can be seen, the weight loss begins gradually up until

200^{o}C, then significant weight loss occurred in the range of 200°C -320°C. The devolatilization behavior of biomass is associated with the presence of cellulose, hemicelluloses and lignin (Raveendran et al., 1996). Biagini et al. investigated the devolatilization of hemicelluloses, cellulose and lignin and they reported the onset temperature of these chemical constituents to be 253°C, 319°C and 253°C, respectively (Biagini et al., 2006). They also observed that the lignin was decomposed in a wider range of temperatures. The weight loss at temperatures < 100°C can be attributed to the loss of easily volatiles, while the weight loss occurring between 100 and 130°C is due to loss of water. The results showed that CM is stable and suitable for butanol dehydration at a bed temperature no higher than 130^{o}C.

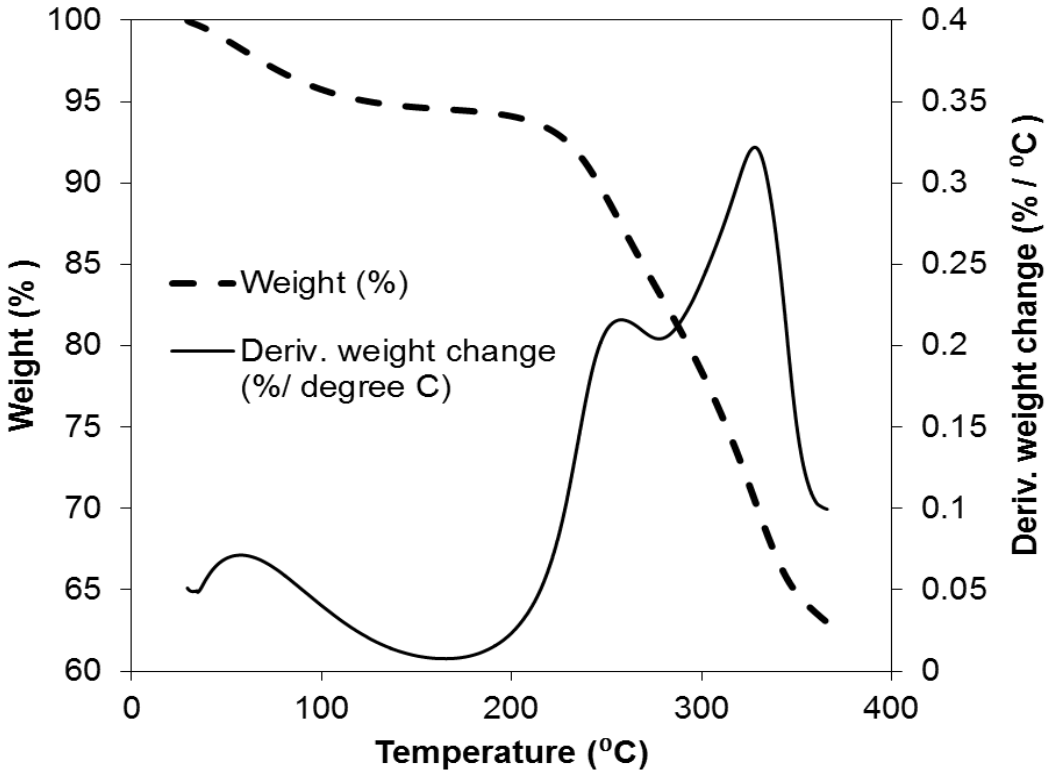


Figure 5.2 TG/DTA analysis of canola meal

Particle size distribution: The particle size distribution of CM initially sieved in the range of 0.43-1.18mm was analyzed by the particle size analyzer. The size analyzer generated the results as volume-based particle size distributions as shown in Fig. 5.3. The results showed that 62 vol% of particle sizes are within the range of 0.47-1.19 mm, 28% are smaller than 0.47 mm and only 9% bigger than 1.19 mm. The median of the size is 0.6 mm. Such particles were used for the following dehydration experiments.

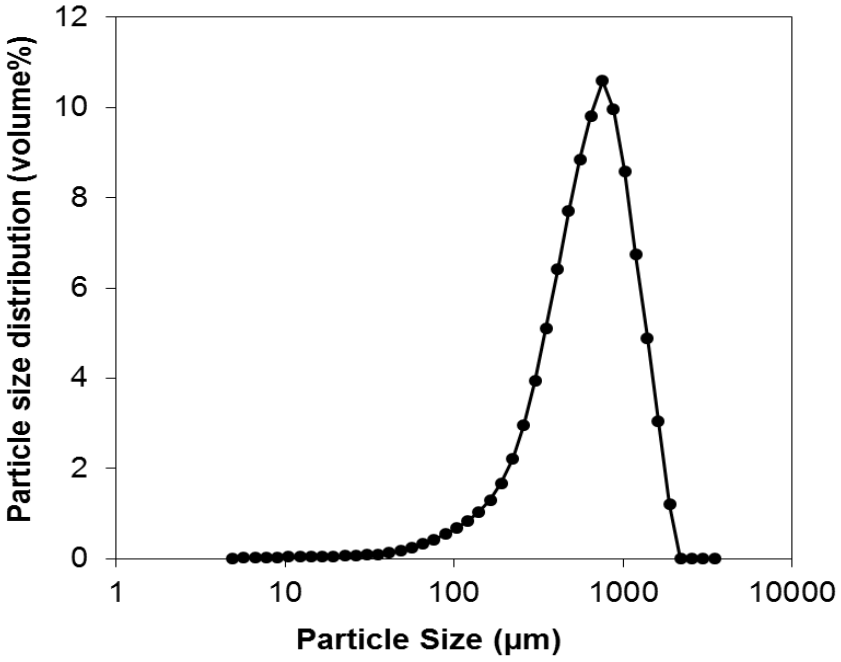
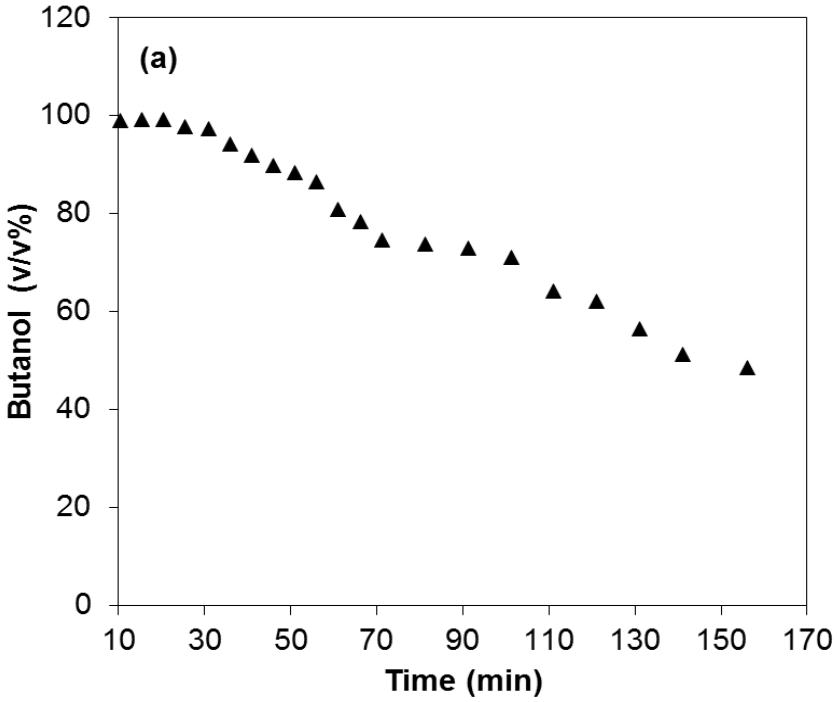


Figure 2.3 Particle size analysis of CM

5.2 Capabilities of CM for drying butanol

Initial experiment was carried out to examine the capability of CM for butanol dehydration at the following conditions: temperature of 111^{o}C; total pressure of 201 kPa; feed butanol concentration of 55 v/v%, feed butanol-water liquid flow rate of 3 mL min^{-1}; and

adsorbent particles size of 0.43-1.18 mm. The butanol and water breakthrough curves are presented in Fig. 5.4a) and 5.4b). The results demonstrated that CM successfully dried a lower grade butanol 55 v/v% and achieved over 99 v/v% fuel grade butanol with a water uptake of 0.42 g g-ads^{-1}. The water uptake by CM was higher than that reported for other cellulosic materials like oak chips (0.28 g/g-ads) and kenaf core (0.23 g/g-ads), in the ethanol dehydration study (Benson and George, 2005). This proves the hypothesis that CM was able to concentrate butanol by selective removal of water, demonstrating a potential for application in butanol drying.



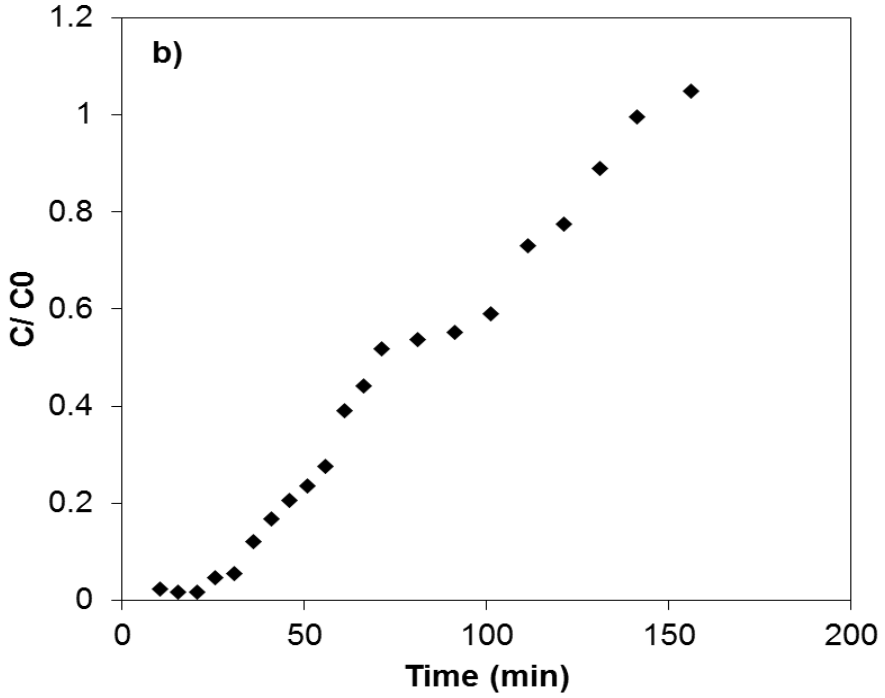


Figure 5.4 Breakthrough curves for canola meal (a) Butanol concentration in the effluent (v/v %) vs. time. (b) Dimensionless water concentration in the effluent C/C0 vs. time

Experimental condition: All runs were at a temperature of 111°C, pressure of 201 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3mL/min and particle size of canola meal in the sieved range of 0.43−1.18 mm.

Thus there is an incentive to further determine the crucial operation parameters and optimize the butanol dehydration using CM as biosorbent.

5.3 Effect of operation parameters on butanol dehydration using CM

In order to optimize the butanol drying process, the orthogonal array design (OAD) tool was used to determine the effects of the selected parameters on butanol dehydration. The OAD tool is believed to be more effective than the common one-factor-at-a-time approach because of having reduced groups of experiments (Medina et al., 2009). Five effective operating variables, namely

temperature (factor A), pressure (factor B), butanol feed concentration (factor C), feed flow rate (factor D) and particle size (factor E) that affect the butanol dehydration process were chosen to be experimentally studied at 2 levels namely L_1 and L_2. The factors are tested in the ranges of 95-111°C, 135-201 kPa, 55-95 v/v%, 1.5-3mL/min and 0.425-1.18mm and 4.7mm, respectively.

The experiments' sequence was randomly carried out to avoid personal or subjective errors and are run in duplicate. The designed experiments were replicated and the resultant average for dehydration indices namely as water uptake, butanol uptake, water selectivity, butanol recovery and maximum achievable butanol concentration were reported with standard deviation. The experimental results and conditions for all 8 set of experiments as shown in Table 5.3.

Table 2.3 Experimental combinations using OAD and the corresponding results

Expt. No.	Factors					Experimental results				
	A	B	C	D	E					
	Temp (°C)	Pressure (kPa)	Inlet Bu-OH Conc. (v/v%)	Inlet flow rate (mL/min)	Particle size (mm)	Water Uptake*	Butanol uptake*	Equilibrium Water selectivity	Recovery (%)	Max. Effluent Bu-OH conc. (v/v %)
1	95	135	55.99 ± 1.03	1.5	0.425-1.18	0.36±0.02	0.21±0.02	1.77±0.03	58.03±3.17	99.17 ± 0.09
2	95	135	55.39±0.14	3.0	4.7	0.16±0.00	0.06±0.02	3.22±0.92	83.56±5.57	96.65 ± 0.01
3	95	201	95.33±0.02	1.5	0.425-1.18	0.02±0.00	0.80±0.00	0.40±0.11	6.88±0.03	88.82 ± 1.89
4	95	201	94.02±0.76	3.0	4.7	0.05±0.01	0.59±0.00	1.05±0.02	15.40±0.17	99.19 ± 0.11
5	111	135	95.72±0.10	1.5	4.7	0.01±0.00	0.11±0.00	1.95±0.10	71.16±0.82	99.13 ± 0.03
6	111	135	94.96±0.06	3.0	0.425-1.18	0.03±0.00	0.25±0.01	2.05±0.03	85.63±0.91	99.17 ± 0.55
7	111	201	56.50±0.33	1.5	4.7	0.14±0.00	0.10±0.00	1.42±0.04	49.79±1.18	93.67 ± 2.44
8	111	201	55.50±0.91	3.0	0.425-1.18	0.64±0.01	0.32±0.11	2.13±0.67	67.48±10.26	98.86 ± 0.41

* g adsorbed/ g dry net weight of adsorbent at equilibrium conditions

5.3.1 Effect of operating parameters on butanol drying

The experimental results from Table 5.3 were further treated by the range analysis to determine the most significant parameters for the butanol dehydration performance. In the range analysis of OAD, the average values of each of the butanol dehydration indices at equilibrium including water uptake, butanol uptake, water selectivity, butanol recovery, and maximum effluent butanol concentration were determined and denoted as k_1 and k_2, respectively for each operating parameter (A, B, C, D, & E). The subscripts of k represent level 1 and 2 of each parameter.

For an example, to determine the effect of temperature on water uptake, the average water uptake obtained at level 1 temperature, i.e. 95^{o}C was calculated and noted as k_1, and that at level 2 temperature 111^{o}C was calculated and noted as k_2. Same treatment was done for all dehydration performance indices and parameters. Table 5.4 summarizes the influence of operating parameters on corresponding performance indices based on the statistical range analysis. Range value, denoted by Δ, was determined by the difference in the maximum and minimum k values obtained for each factor (Ou et al., 2015; Sharma et al., 2005; Wu et al., 2012).

Specifically in this work there are only two levels for each factor, Δ is thus determined as follows:

$$\Delta = | k_1 - k_2 | \quad (5.1)$$

Ranking was then done in the order of the highest to the lowest range values for each performance index. The highest ranked factor (i.e. 1) had the most significant effect, while the lowest ranked factor (5) had the least effect on the process of dehydration (Medina et al., 2009; Sharma et al., 2005; Wu et al., 2012). The larger the Δ value of a parameter, the higher the rank

of the parameter in the process. The parameter having the largest Δ value and the highest rank for a performance index has the most significant effect on that specific index.

Table 5.4 Results of Range analysis

Water Uptake					
Mean values	A	B	C	D	E
k1	0.15	0.18	0.26	0.13	0.19
k2	0.01	0.03	0.03	0.1	0.07
Δ	0.14	0.15	0.23	0.03	0.12
Rank	3	2	**1**	5	4
Butanol Uptake					
Mean values	A	B	C	D	E
k1	0.29	0.13	0.17	0.14	0.27
k2	0.18	0.34	0.35	0.32	0.22
Δ	0.11	0.21	0.18	0.18	0.05
Rank	3	**1**	2	2	4
Water Selectivity					
Mean values	A	B	C	D	E
k1	1.61	2.25	2.14	1.39	1.59
k2	1.89	1.25	1.36	2.11	1.91
Δ	0.28	1	0.78	0.72	0.32
Rank	5	**1**	2	3	4
Butanol Recovery					
Mean values	A	B	C	D	E
k1	40.96	74.6	64.72	46.47	54.51
k2	68.52	34.89	44.77	63.02	54.98
Δ	27.56	39.71	19.95	16.55	0.47
Rank	2	**1**	3	4	5
Maximum Effluent Butanol Concentration					
Mean values	A	B	C	D	E
k1	95.96	98.53	97.24	95.2	96.5
k2	97.7	95.13	96.58	98.6	97.16
Δ	1.74	3.4	0.66	3.4	0.66
Rank	2	1	3	1	3

A Temperature (°C); **B** Pressure (kPa); **C** Feed butanol Conc. (v/v%)

D Feed butanol-water liquid flow rate (mL/min); **E** Particle size (mm)

As per the range analysis of water uptake shown in Table 5.4, the feed butanol concentration (C) having the highest Δ value indicated that it was the most significant influencing factor for the water uptake. At the level 1 of the butanol feed concentration being 55 v/v%, the average water uptake k_1 was 0.26 g/g-ads; while at level 2, 95 v/v% butanol, water uptake k_2 was significantly decreased to 0.03 g/g-ads.

Pressure (B) was found to be the second most important factor affecting water uptake. Temperature (A) in the tested range had the next significant effect on water uptake. The higher the temperature, the lower the water uptake, which confirmed the exothermic nature of water adsorption. Feed liquid flow rate (D) and particle size (E) in the tested ranges had less effects on water uptake.

In regard to butanol uptake, pressure was found to be the most significant parameter affecting it, followed by feed butanol concentration, temperature, feed liquid flowrate and particle size (Table 5.4). Butanol uptake was found to be increased from 0.13 g/g-ads to 0.34 g/g-ads when the pressure increased from 135 to 201 kPa. As lesser butanol uptake was preferred in the present study with a selective water adsorption approach, lower pressure of 135 kPa was found to be optimum over a higher pressure of 201 kPa. Butanol feed concentration and feed liquid flow rate were observed to have a similar effect on butanol uptake and they collectively were ranked as the second most important factors. For a preferential lower butanol uptake, lower values of the above two parameters were found to be optimum. With the third significant factor being the temperature, it was seen that as temperature was increased from 95 to 111°C, butanol uptake decreased from 0.29 g/g-ads to 0.18 g/g-ads, which indicated the exothermic nature of butanol adsorption. Chang et al., (2006b) reported that with increasing temperature at constant pressure and vapor feed concentration, ethanol uptake decreases rapidly compared to water

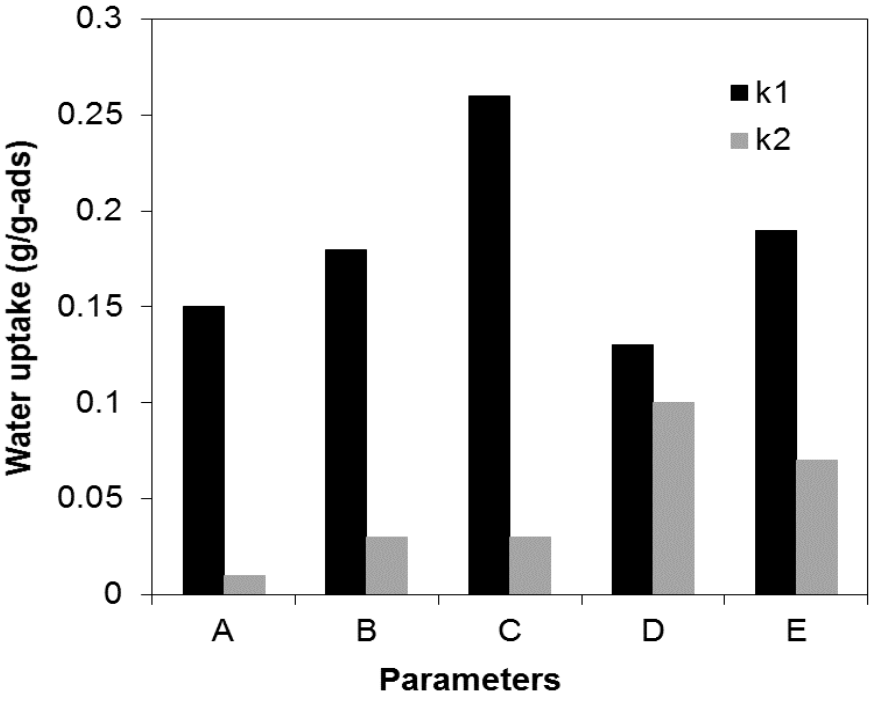
uptake. In addition, the solubility of a substance determines its chemical potential, which in turn controls adsorption. When the solubility of the adsorbate increases with increasing temperature, adsorption is decreased and vice versa. In most cases, physical adsorption decreases with increasing temperature (Lin et al., 2012a) and the same pattern was observed in the present study. Particle size in the tested range was observed to have least influence on butanol uptake.

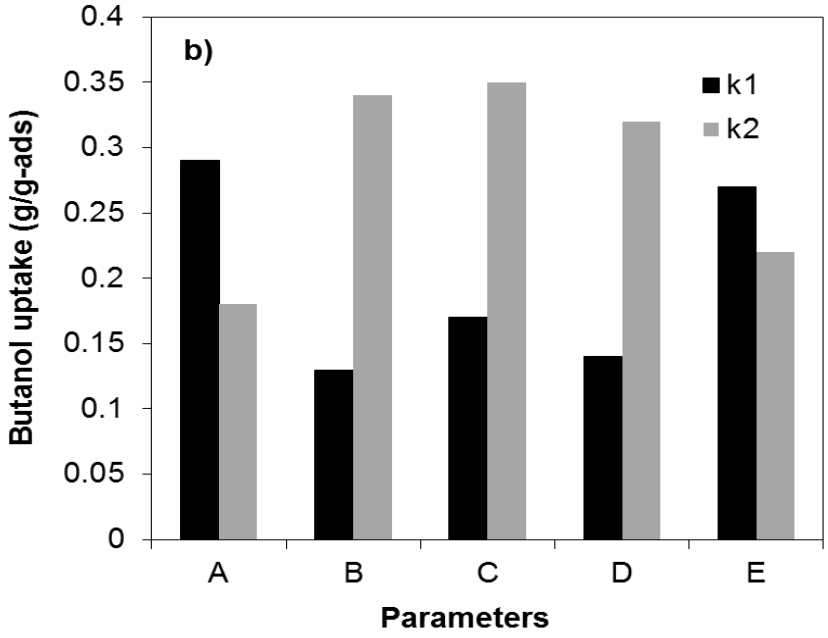
Water selectivity is a very critical process performance criterion in adsorption, as it translates to the preferred adsorptive species over the undesired (Ruthven, 1984). The higher the water selectivity, the better the performance of dehydration process. Pressure was found to be the most crucial factor affecting water selectivity (Table 5.4). Lower pressure of 135 kPa resulted in a higher water selectivity of 2.25 (Table 5.3). Butanol feed concentration was the next significant influencing factor for selectivity. At a lower butanol feed concentration of 55 v/v%, a higher water selectivity of 2.14 was obtained. Chang et al. (2006) also observed that with increased ethanol feed concentration, water adsorption selectivity by cornmeal decreased. Feed liquid flow rate was seen to be the third important factor and at a higher feed flow rate of 3 mL min^{-1}, a higher selectivity of 2.11 was obtained. Particle size and temperature did not seem to have significant impact on selectivity under the tested range of conditions. Vareli et al., (1998) studied the adsorption of water and ethanol on wheat straw with two different ranges of particle sizes - 80–100 and 100–120 mesh and also observed similar water selectivity (water separation factors) obtained at the two ranges of particle sizes.

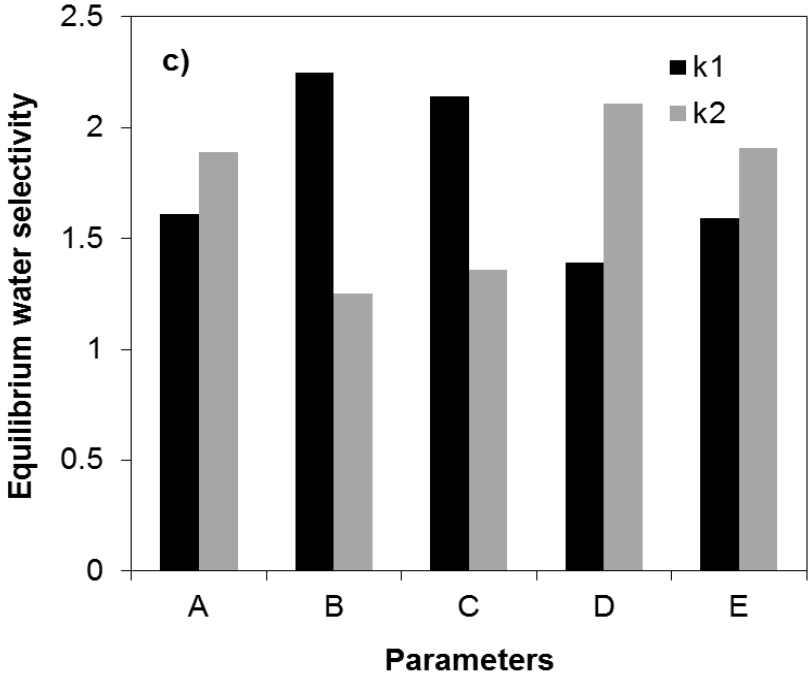
Maximizing butanol recovery is one of the primary targets in selective water adsorption process. As per the range analysis in Table 5.4, it was found that pressure was the most significant factor affecting butanol recovery. At a lower pressure of 135 kPa, a higher butanol recovery of about 75% was obtained compared to only 35% recovery at 201 kPa. In order to

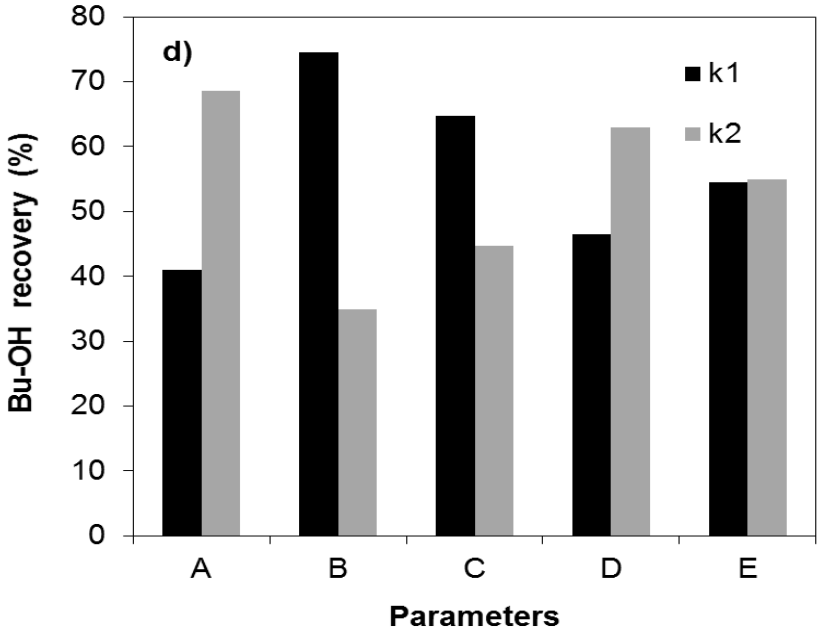
obtain a high butanol recovery, a lower pressure is preferred. The second most influential factor was temperature followed by feed butanol concentration, and feed liquid flow rate. At a higher bed operation temperature, lower feed butanol concentration, and higher liquid feed flow rate, a relatively high butanol recovery was obtained. Chang et al., (2006b) have also stated that productivity (recovery) increases with increased ethanol concentration, but start to decrease at higher ethanol concentrations because of increased resistance to diffusion of water through ethanol. The particle size within the tested range was again found to have an insignificant role on butanol recovery.

The primary purpose of a selective water adsorption process is to obtain high purity butanol as a direct end product from a low titer butanol. Pressure and feed liquid flow rate were found to have the most significant influence on the maximum effluent butanol concentration (Table 5.4). A lower pressure of 135 kPa and a higher feed flow rate of 3 mL min^{-1} resulted in 98.4 v/v% butanol concentration from as low as 55 v/v% butanol concentration (Table 5.4). Temperature was the second most influential factor but the resultant butanol concentration at the tested temperatures were only slightly different from each other; being 95% and 98% recovery at 95°C and 111°C, respectively. Butanol feed concentration and particle size also had least effects on this index.


0.3
0.25
0.2
0.15
0.1
0.05
0
Water uptake (g/g-ads)
k1
k2
A
B
C
D
E
Parameters


b)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Butanol uptake (g/g-ads)
k1
k2
A
B
C
D
E
Parameters


c)
k1
k2
Equilibrium water selectivity
2.5
2
1.5
1
0.5
0
A
B
C
D
E
Parameters


d)
k1
k2
Bu-OH recovery (%)
80
70
60
50
40
30
20
10
0
A
B
C
D
E
Parameters

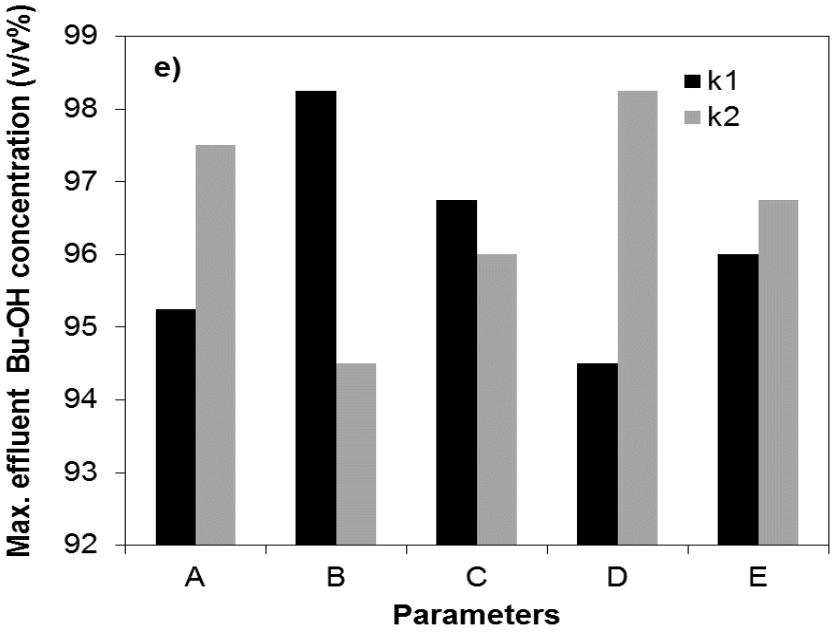


Figure 5.5 Graphical depiction of range analysis for each index. a) Effect of factors on water uptake. b) Effect of factors on Bu-OH uptake. c) Effect of factors on selectivity. d) Effect of factors on Bu-OH recovery. e) Effect on maximum Bu-OH concentration

5.3.2 Determination and validation of optimum operating conditions for Bu-OH drying

Based on the above statistical range analysis, the importance of a given factor on the output indices was determined so as to optimize the dehydrating process conditions. For that end, a set of optimum conditions were proposed, again by the range analysis, i.e. the Rank is determined based on the range values (Δ) obtained and was given in the order of descending range values. The highest ranked factor thus has the most significant influence on that specific output index. The higher the rank, the larger the effect the variable has on the process, similar approach to that was done for nickel adsorption (Ou et al., 2015).

The decisions about optimum operating conditions are based on desirable results of output indices namely: high water uptake, low butanol uptake (since the study targets selective

water adsorption over butanol), high selectivity, high recovery and high maximum effluent Bu-OH concentration.

Based on the above results determining the significant factors, in the case of water uptake index, according to Table 5.4, it's seen that Δ value for inlet butanol concentration (factor C) is the highest of all range values and hence been ranked '1', indicating that factor C has a significant impact on water uptake than other factors. The other factors are ranked in the order of descending range values: pressure, temperature, particle size and liquid feed flow rate. Also, the average water uptake values for factor C at different level shows that, k_1 is 0.26 g/g-ads and k_2 is 0.03 g/g-ads. Hence apparent that, factor C at level 1 has contributed to a higher water uptake than at level 2. Hence inlet butanol feed concentration at level 1, that is 55 v/v%, is preferred as it results in a higher water uptake.

From the range analysis for butanol uptake index, according to Table 5.4, it's seen that Δ value for Pressure (factor B) is the highest of all range values of other factors and thus ranked rank 1. As the research approach is to only target water and not butanol adsorption, only a lower butanol uptake is preferred. This is key to find the optimum condition for pressure. A much closer look at the average butanol uptake values for factor B at different level shows that, k_1 is 0.13 g/g-ads and k_2 is 0.34 g/g-ads. This is indicative that factor B at level 2 has contributed to a higher butanol uptake than at level 1. Hence pressure at level 1, that is 135 kPa, is preferred as it results in lower butanol uptake.

In the same way, considering the range analysis for indices of water selectivity, butanol recovery and maximum effluent butanol concentration, it's seen that the Δ range values of factor B is the highest of all and been ranked '1'. It means that pressure (factor B) has a very significant

impact on all the output indices. It could also be attributed to the fact that a pressure swing adsorption approach was deployed.

The average water selectivity values for its most significant factor pressure (factor B) shows that k_1 is 2.25 and k_2 is 1.25. It implies that factor B at level 1 has led to to a higher water selectivity than at level 2. Hence pressure at level 1, which is 135 kPa is preferred. The average butanol recovery values for pressure (factor B) from Table 5.4 shows that k_1 is 74.60% and k_2 is 34.89%. It shows that factor B at level 1 has contributed to a higher butanol recovery than at level 2. Hence pressure at level 1, which is 135 kPa is preferred. The average maximum effluent butanol concentration values for factor B shows that k_1 is 98.53 v/v% and k_2 is 95.13 v/v%. It shows that factor B at level 1 has led to a higher effluent butanol concentration than at level 2. Hence pressure at level 1, which is 135 kPa is preferred.

Interestingly, from the range analysis of the maximum butanol concentration in effluent index, the range values for temperature (factor B) and liquid feed flow rate (factor D) are the same and are the highest amongst others. The average maximum effluent butanol concentration values for factor D shows that k_1 is 95.20 v/v% and k_2 is 98.6 v/v%. It indicated that factor D at level 2 has contributed to a higher effluent butanol concentration than at level 1. Hence liquid feed flow rate (factor D) at level 2 is preferred, which is 3 mL/min.

Thus optimum operating conditions for pressure, inlet butanol concentration and liquid feed flow rate were found directly from the analysis above as 135 kPa, 55 v/v% and 3mL/min respectively.

Decisions were made to optimize temperature (factor A) by looking at the range and average values of water selectivity, butanol recovery and maximum effluent butanol concentration. The average water selectivity values for temperature (factor A) shows that k_1 is

1.61 and k_2 is 1.89. It shows that the temperature at level 2 has contributed to a higher water selectivity than at level 1. The average butanol recovery values for temperature shows that k_1 is 40.96% and k_2 is 68.52%. It indicated that temperature at level 2 has contributed to a higher butanol recovery than at level 1. Similarly, the average maximum effluent butanol concentration values for temperature shows that k_1 is 95.96 v/v% and k_2 is 97.70 v/v%. Again, it shows that temperature at level 2 has contributed to a higher maximum effluent butanol concentration than at level 1. Hence temperature at level 2 is preferred, which is 111° C.

Decisions were made to optimize particle size (factor E) by looking at the range and average values of water uptake index. The average water uptake values for particle size shows that k_1 is 0.19 and k_2 is 0.07. It shows that factor E at level 1 has contributed to a higher water uptake than at level 2. Hence particle size at level 1 is preferred, which is 0.425-1.18mm.

Water uptake is the key component for calculations of water selectivity and maximum effluent butanol concentration. Thus the particle size of 0.425-1.18mm is chosen over 4.7mm pellets; smaller particle size also provides larger surface area for adsorption and thus the particle size chosen is reasonable.

In summary, based on the above analysis, a set of optimum conditions for butanol dehydration were proposed in order to achieve higher water uptake, lower butanol uptake, higher water selectivity, higher butanol recovery and higher butanol concentration in the effluent. The specific conditions are as follows: temperature of 111°C, pressure of 135 kPa, butanol concentration of 55 v/v/%, feed flow rate of 3 mL min^{-1}, and particle size of 0.425-1.18 mm, which otherwise can be defined in terms of design factors and levels as **A2B1C1D2E1**.

Validation: Since the above proposed optimum conditions were proposed by the range analysis and were not included in the original OAD design (Table 4.1), in order to confirm their

validity, the experiment was carried out in duplicate at the above mentioned conditions. The average results are presented in Table 5.5 and Fig.5.6 a-b). The results show that CM particles successfully concentrated butanol from 55 v/v% to 99 v/v% with a water uptake of 0.48 g/g-ads. Apparently, a higher water selectivity of 5.43, butanol recovery of 90%, and a maximum effluent butanol concentration of 99.2 v/v% were achieved in the validation runs using CM particle size of 0.425-1.18 mm.

The results are better than that obtained at any other conditions investigated in this work. The result confirmed that the optimum conditions proposed based on the range analysis is reasonable.

Table 5.5 Validation test results for the most optimum process conditions for drying of butanol

Water uptake (g/g-ads)	Butanol uptake (g/g-ads)	Water selectivity	Recovery (%)	Max. Butanol concentration achieved (v/v %)
0.48±0.02	0.09±0.00	5.43±0.08	90.11±0.26	99.20 ±0.79

As shown in the range analysis table of 5.4, the average values k of all the indices namely water uptake, butanol uptake, equilibrium water selectivity, butanol recovery and maximum butanol concentration in effluent for particle size (factor E) were consistently low and thus factor E was ranked low. This implied that particle size in the tested range had negligible effects on butanol uptake, water selectivity, butanol recovery and maximum effluent butanol concentration. Because particle size is usually important to affect adsorption rate, further study was done to investigate the effect of particle size on butanol dehydration rate.

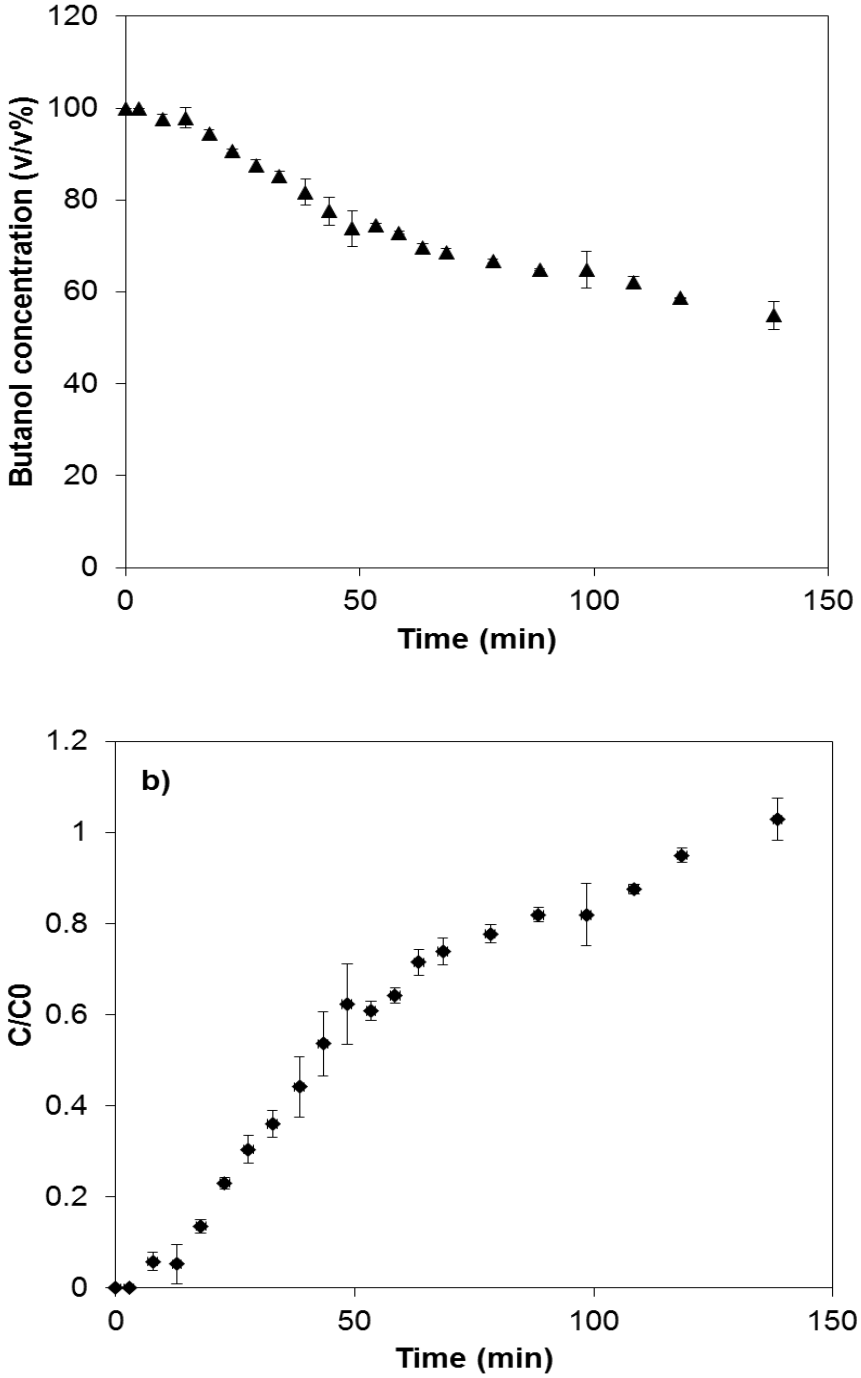


Figure 5.6 Breakthrough curves for validation experiment with 0.425-1.18mm canola meal particles (a) Butanol concentration in the effluent (v/v%) vs. time. (b) Dimensionless water concentration in the effluent C/C0 vs. time

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3mL/min and particle size of canola meal in the range of 0.43-1.18 mm

Particle sizes of both 0.425-1.18 mm and 4.7mm pellets were investigated with newly determined optimum conditions at temperature of 111°C, pressure of 135 kPa, butanol concentration of 55 v/v/%, feed flow rate of 3 mL min^{-1}. Fig. 5.6 showed the water breakthrough curve and butanol profile in the effluent in the case of particle sizes of 0.425-1.18 mm. Fig. 5.7 further compared the butanol profiles in the effluent with both of the particle sizes, namely 0.425-1.18mm and 4.7mm pellets. It's clear that the butanol breakthrough curves obtained from experimental runs with both 0.425-1.18mm and 4.7 mm pellets almost overlapped. The slopes of the breakthrough curves indicate the mass transfer rate was similar. Although the butanol concentration in the effluent dropped slightly faster at the late stage in the case of 4.7 mm pellets, both the adsorption processes reached equilibrium at similar time. In addition, both particle sizes led to similar water selectivity of 5.25, butanol recovery of 90%, and a maximum effluent butanol concentration of 99 v/v% as shown in Table 5.6. These results not only demonstrated that the particle size in the tested range had an insignificant effect on the overall dehydration process, but also that the optimum condition chosen based on the range analysis is reasonable.

Table 5.6 Particle size effect results using 0.425-1.18mm CM particles and 4.7mm CM pellets

Adsorbent Particle size	**Water uptake (g/g-ads)**	**Butanol uptake (g/g-ads)**	**Water selectivity**	**Butanol recovery (%)**	**Max. Effluent butanol concentration achieved (v/v %)**
0.425-1.18 mm	0.48 ± 0.02	0.09 ± 0.00	5.43 ± 0.08	90.11 ± 0.26	99.20 ±0.79
4.7mm	0.47 ± 0.01	0.04 ± 0.06	5.25 ± 0.28	89.67 ± 0.68	98.86 ±0.67

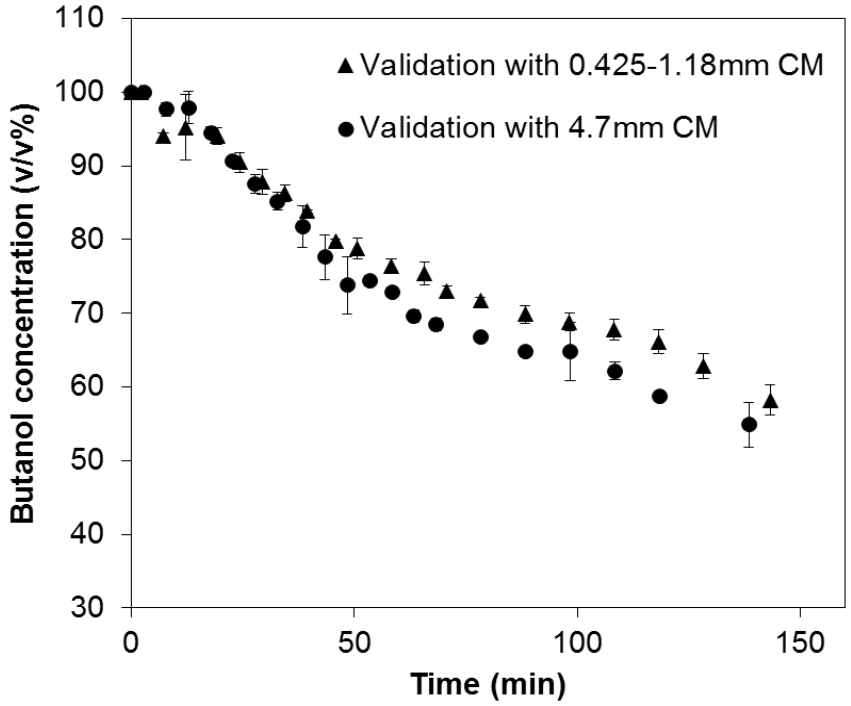


Figure 5.7 Butanol breakthrough curves for experiment run with 0.425-1.18mm CM particles and 4.7mm CM pellets

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3mL/min and particle size of canola meal in the range of 0.43-1.18 mm and 4.7mm pellets

5.4 Water Adsorption Equilibrium Using CM as Biosorbent

In this work, all data for water adsorption equilibrium were achieved when the adsorption column packed with CM reached saturation. The water adsorption isotherms were obtained at temperatures of 95, 100 and 111°C and the water feed concentrations in the range of 5-45 v/v% corresponding to 95 – 55 v/v/% butanol. The pressure of the system was maintained at 135 kPa, and the feed liquid flow rate was held at 3 mL/min. The adsorbent particle size chosen for this study was 0.425-1.18 mm. Although there are many isotherm models, the Dubinin-Polanyi model based on adsorption potential theory has been found to give the most reasonable

representation of the equilibrium isotherm data in this study. A similar kind of modelling approach was done on water adsorption equilibrium on carbon nanomaterials (Yang et al., 2006), corn meal (Chang et al., 2006b), modified rice husk (Dada et al., 2012) and canola meal (Ranjbar et al., 2013).

The Dubinin-Polanyi model used in this work is based on adsorption potential theory, which has been recognized as the useful model for dealing with both gas and aqueous adsorption on energetically heterogeneous surfaces such as biomass. As per this model, for any molecule, the magnitude of adsorption potential varies within the adsorption space depending on its proximity to the atoms on the adsorbent surface (Polanyi, 1920). Polanyi theory assumes that the adsorption potential, ε is independent of temperature and the adsorbed gas phase molecules have the similar properties as the corresponding bulk gas phase (Chang et al., 2006a). Meanwhile, the adsorption potential ε is given by,

$$\varepsilon = \mathrm{RT} \ln \left(\frac{P^s}{P_i}\right) \tag{5.2}$$

The Dubinin–Polanyi equation for microporous and large pore materials is described in eqs.5.3 and 5.4 respectively as shown below.

$$\ln q = \ln q_0 - \frac{K_1}{\beta} \left[\mathrm{RT} \ln \left(\frac{P^s}{P_i}\right) \right]^2 \tag{5.3}$$

$$\ln q = \ln q_0 - \frac{K_2}{\beta} \left[\mathrm{RT} \ln \left(\frac{P^s}{P_i}\right) \right] \tag{5.4}$$

where q is the mass adsorbed per unit mass of adsorbent (g adsorbed/g adsorbent), q_0 denotes the limiting mass for adsorption (g adsorbed/g adsorbent), K_1 and K_2 are pore constants for micropore and large pore materials, β is an affinity coefficient, P_i represents partial pressure of

the adsorbate (kPa), and P^s is saturated vapor pressure of the adsorbate (kPa). These relationships can be helpful to estimate the adsorption capacity and affinity, and to evaluate the potential application of CM as sorbents. The plot of mass adsorbed (q, g adsorbed/g adsorbent) against equilibrium adsorption potential (ε) yields a characteristic curve as shown in Fig. 5.8.

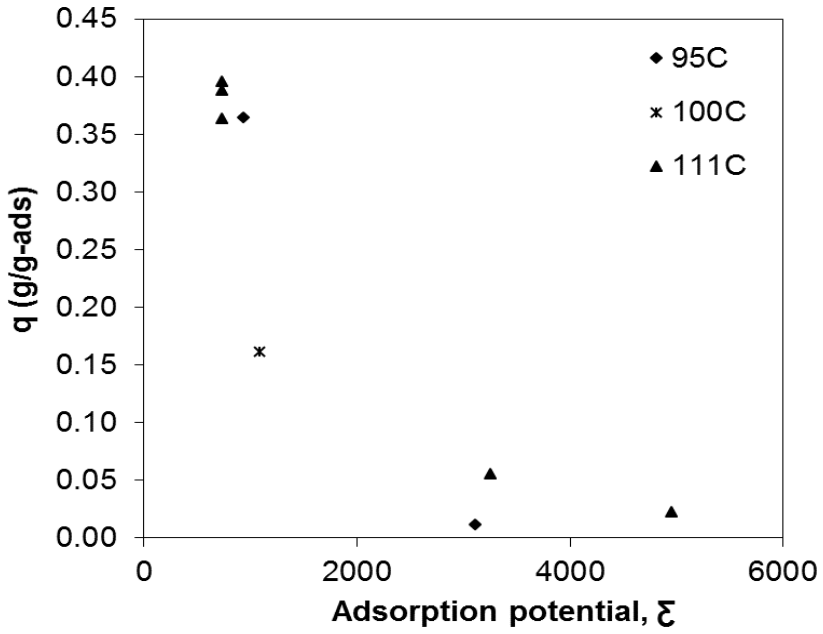


Figure 5.8 Characteristic Curve for Polanyi model

Experimental condition: All runs were at a temperature of 95°C, 100°C and 111°C, pressure of 135 kPa, butanol feed concentration of 55-95 v/v %, feed flow rate of 3mL/min and particle size of canola meal in the range of 0.43-1.18 mm

A series of equipotential surfaces can be obtained once the points in adsorption space with the same ε are connected. This type of similar temperature-invariant characteristic curve was observed for the polycyclic aromatic hydrocarbons (PAH) adsorption by carbon nano particles (CNPs), which indicates that Polanyi theory also captures the gas adsorption process mechanistically (Yang et al., 2006). The above eqs. 5.3 and 5.4 were used to fit the equilibrium

water adsorption data in this work. The resultant graphs are presented as Fig.5.9 and Fig.5.10, respectively.

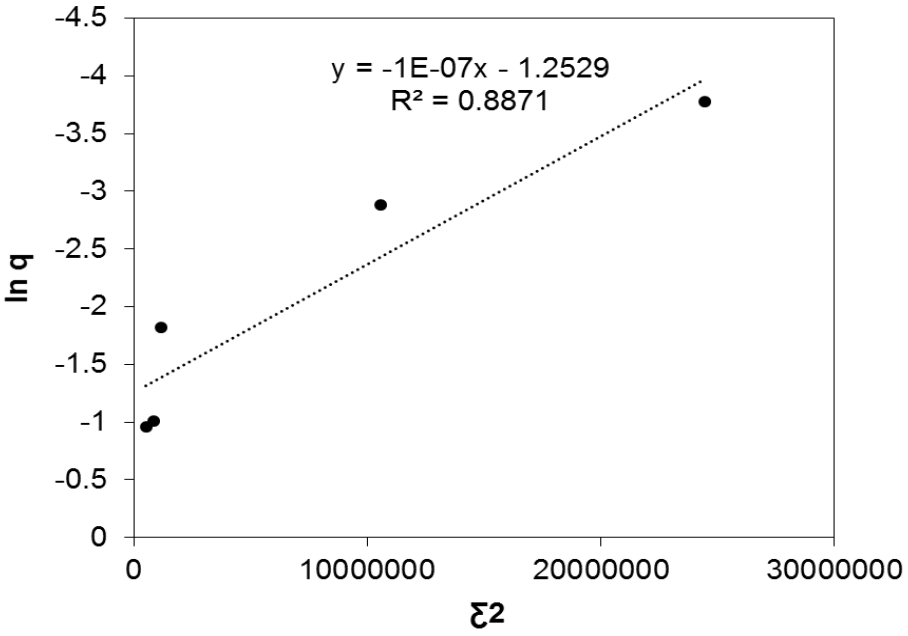


Figure 5.9 Dubinin−Polanyi model for micropore materials: (●) experimental data; (−) model

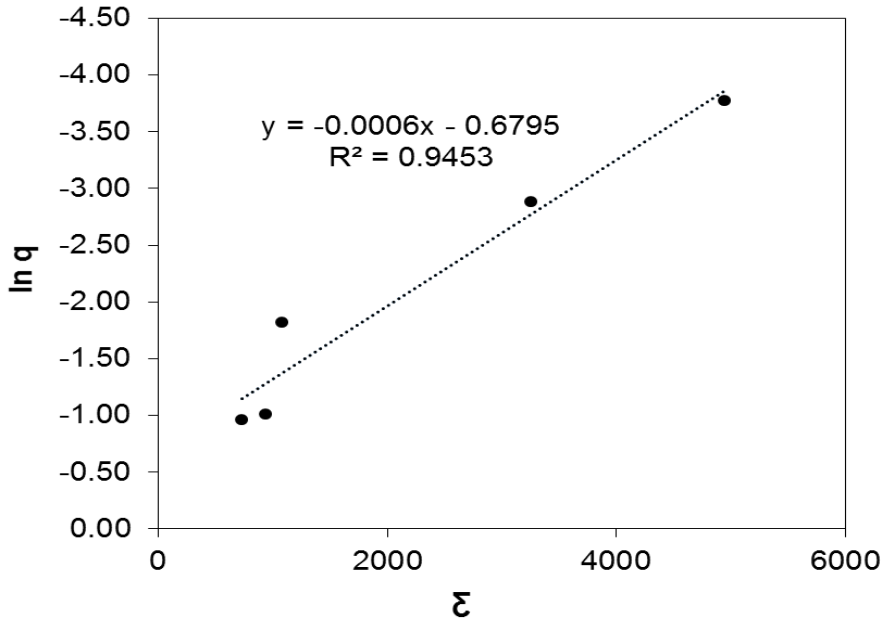


Figure 5.10 Dubinin−Polanyi model for large pore materials: (●) experimental data; (−) model

Table 5.7 summarizes the Dubinin-Polanyi model parameters for the micropore and large pore materials. As it can be seen, eqn. 5.4 representative of large pore materials gave a better fit compared to eqn. 5.3. Similar modeling results were obtained for ethanol dehydration by canola meal (Ranjbar, et al., 2013). However, elucidation of actual adsorption mechanisms require further investigation.

According to eq. 5.4, the values of the limiting mass for adsorption (q_o) and the coefficient $\frac{K_2}{\beta}$ were estimated from the intercept and slope to be 50.68% and 6 x 10^{-4}, respectively. (Chang et al., 2006b) reported these values to be 16.33% and 3.28 x 10^{-4} and (Ranjbar et al., 2013) reported these to be 69.59% and 4 x 10^{-4}, in an ethanol-water binary vapor system using corn meal and canola meal as adsorbents respectively.

Table 5.7 Modeling results of Dubinin-Polanyi equations

Model Type	K/β	Energy of adsorption (kJ/mol)	q_0 (g/g-ads)	Heat of Adsorption(kJ/mol)	r^2	ARE % *
Micropore in this work	1E-07	2.24	0.29	-2.23	0.89	11
Large pore in this work	6E-04	0.02	0.51	-28.86	0.95	3.5
Canola meal for drying ethanol (Ranjbar et al., 2013)	4E-04	0.04	0.69	-35.81	0.97	5
Corn meal for drying ethanol (Chang et al., 2006a)	3E-04	0.04	0.16	-	0.96	-

*ARE - Average Relative Error

The mean free energy of adsorption was evaluated using the following equation:

$$E = \frac{1}{\sqrt{2\frac{K_2}{\beta}}} \quad (5.5)$$

The value of the mean free energy is an indication of the nature of the adsorption process. For those values of E between 8 and 16 kJ/mol, the adsorption process is considered to be chemisorption while the process is physisorption for the values of E lower than 8 kJ/mol (Dang et al., 2009). The mean free energy obtained in this work for the large pore model was 0.02, indicating the water adsorption is physisorption. It is consistent with water adsorption studies on corn meal (Chang et al., 2006b) and canola meal (Ranjbar et al., 2013) as shown in Table 5.7.

The thermodynamic parameters such as heat of adsorption, Gibb's free energy change and entropy change are important in order to understand the adsorption process. The Gibb's free energy ΔG° indicates the degree of spontaneity of the adsorption process and is given by the following equation (El Haddad, 2012):

$$\Delta G° = \Delta H° - T\,\Delta S° \quad (5.6)$$

$$(-RT)\ln K = \Delta H° - T\,\Delta S° \quad (5.7)$$

$$\ln K_o = (-\Delta H°/R) * (1/T) + \Delta S°/R \quad (5.8)$$

where ΔH° is the enthalpy change (adsorption heat) (kJ/mol), ΔS° the entropy change (J/mol K), T the absolute temperature (K), R is universal gas constant (8.314 J/mol K), ΔG° Gibb's free energy (kJ/mol) and K_o is the equilibrium constant of the adsorption process at temperature T. A plot of ln (q_e/C_e) as a function of C_e at a specific temperature gives lnK_o by extrapolating it to

zero C_e (Khan and Singh, 1987; Meng et al., 2015), where q_e and C_e are the equilibrium water uptake (g/g), and water concentration in the vapor phase, respectively.

ΔH° and ΔS° values were obtained from the slope and intercepts of the plot of lnK_o versus 1/T as shown in Table 5.8. ΔG° is calculated for different temperatures (95, 100, 111^{o}C) using eqn.5.6. The Gibb's free energy change for this adsorption study was found to be negative which confirms that the adsorption process occurs spontaneously in forward direction. Also, the entropy change value ΔS° and enthalpy change ΔH° were found to be 513.46 J/mol and -184.35 kJ/mol.

Table 5.8 Thermodynamic Parameters for Water Adsorption on CM

ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)		
		95 °C	100 °C	111 °C
-184.346	513.464326	-373.13	-375.695	-381.338

The positive ΔS° value indicated the increased randomness at the gas-solid interface during adsorption. A negative ΔH° indicates the exothermic nature of adsorption which is consistent to the fact of bed temperature increase during adsorption in this work. For an example, when the operation temperature was at 111^{o}C, as the water adsorption went on, a sharp increase in bed temperature was observed, as shown in Fig 5.11. This confirmed the adsorption is an exothermic process. The heat generated from the adsorption could not be removed instantly by the oil jacket so that the bed temperature increased. When the column was saturated (adsorption reached equilibrium), the bed temperature decreased.

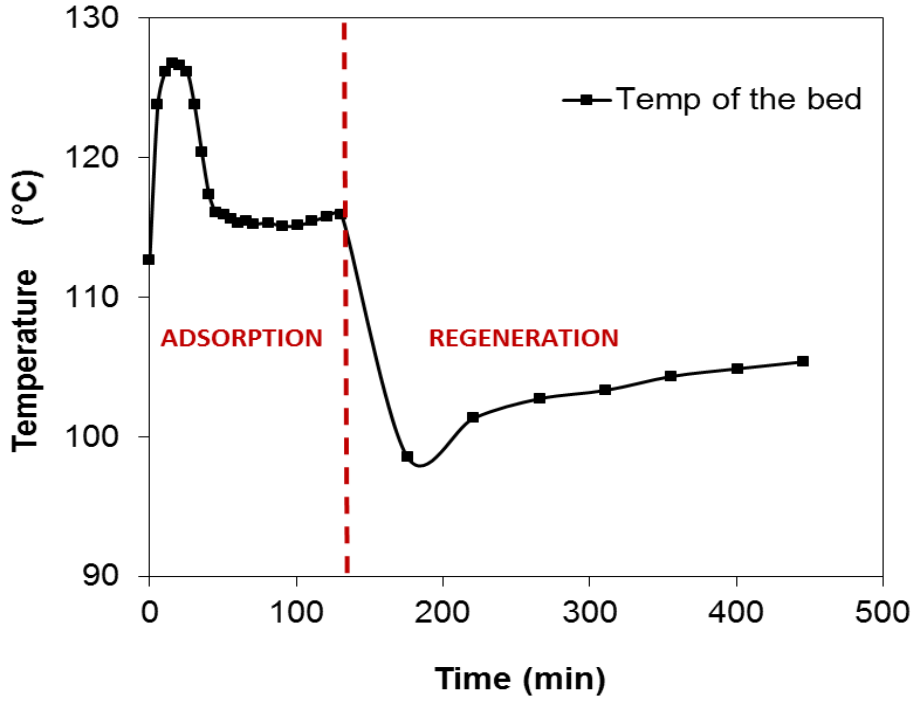


Figure 5.11 The average bed temperature profile during adsorption-desorption cycle in PSA

Experimental condition: temperature of 111°C, average standard deviation of the temperature is 2.6°C, pressure of 135 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3 mL/min and particle size of canola meal in the sieved range of 0.43−1.18 mm.

5.5 Regeneration and Adsorbent Stability

After saturated in the butanol dehydration process, the CM packed column was successfully regenerated for reuse. It is essential to ensure that the bed has been sufficiently regenerated for the next cycle of adsorption. In this work, the adsorbent was regenerated at a temperature of 110°C by applying vacuum of 33 kPa with nitrogen purging from the bottom of the column at 850 mL min^{-1} for 5.5 h. The temperature profile is shown in Fig. 5.11. During the regeneration process, initially, the temperature decreased, indicating that water desorption is an endothermic process. After a while, when the water content in the bed decreased, the temperature started

increasing until the initial bed temperature was attained. A similar trend was reported (Simo, 2008) for regeneration of type 3A molecular sieves for ethanol dehydration. At the tail end of the regeneration process, desorbed water species along with little amount of butanol was condensed into a volumetric flask which could further be recycled as feed for subsequent adsorption columns at an industrial scale. Although butanol is of low order human toxicity, the carrier gas-nitrogen that carries desorbed butanol in it can be safely used for recycle rather than vented out, which will also reduce the material costs. Currently, for each batch of the regeneration, 284 L/min N_2 was consumed. Further research in reuse the nitrogen gas is necessary. However, this work is considered for future investigation.

The adsorbent was examined for 16 cycles and are still used without deteriorated quality. Fig.5.12 shows examples of the butanol production profiles of fresh, and regenerated CM for the 1^{st}, 2^{nd} and 3^{rd} reuse. All the curves are overlapped showing that the fresh and regenerated CM biosorbent have similar performance, and are capable of producing fuel grade butanol of over 99 v/v%. CM was reused without any reduction in adsorption capacity. Table 5.2 showed that the elements composition of fresh and regenerated CM are very much similar, once again confirming CM is stable after regeneration.

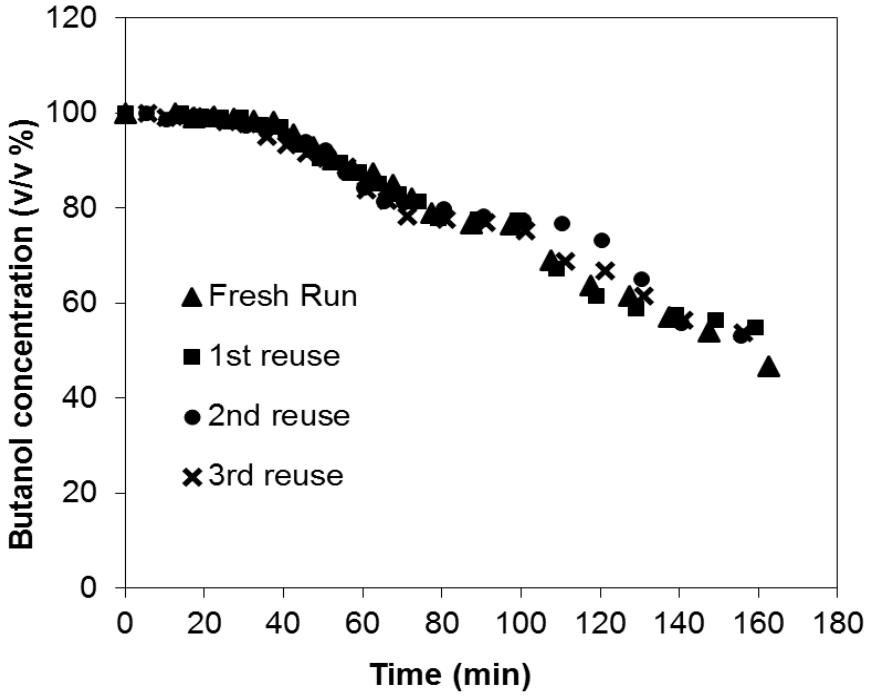


Figure 5.12 Butanol breakthrough curves to evaluate reusability of CM as adsorbent

Experimental condition: All runs were at a temperature of 111°C, pressure of 201 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3mL/min and particle size of canola meal in the sieved range of 0.43−1.18 mm.

The results demonstrated that CM was easily regenerated at 110°C, a temperature much lower than that required for regenerating molecular sieves commonly used in dehydration in ethanol production industry, around 220°C-240°C (Simo, 2008). In addition, the water selective adsorption approach was unlike the butanol selective adsorption approach that normally has regeneration issues like sequential heating desorption method at high temperature leading to adsorbent damages, incomplete butanol recovery (Qureshi et al., 2005) and use of an external agent like methanol for regeneration (Yang et al., 1994).The high water uptake capacity, coupled with lower regeneration temperature, and a relatively easy disposal makes CM to be a promising material for drying butanol vapor.

5.6 Contribution of the major components of CM to butanol dehydration

CM is a multi-component material. To better understand the mechanism of selective water adsorption of CM, it is important to investigate the contribution of the major components of CM towards butanol dehydration. It can also help comprehend and differentiate the cumulative effect from the individual effect. A comparative study of dehydration of butanol on different material fractions also helps to determine the most effective component(s) which may be used in the future for improving an existing biosorbents or develop a novel biosorbents targeted to increase the water uptake and separation factor, and thereby achieve a higher butanol concentration from a lower butanol titer thus a higher productivity. In the ethanol dehydration process, it was demonstrated that cellulose (Al-Asheh et al., 2004; Benson and George, 2005), and protein (Hong et al., 1982; Ostroff et al., 1988) has important roles in water adsorbing capabilities. A similar fractional component study was done on corn meal (Hong et al., 1982) for ethanol dehydration where the relative contributions of three major components of corn meal (starch, xylan and protein) were examined individually. As discussed in the previous section, in this work, the CM material mainly contains cellulose and protein. The performance of the two materials for butanol dehydration was not done yet. Thus, cellulose (C-6288 Sigma) and protein (S-9633 Sigma) purchased from Sigma Aldrich Ltd. were examined individually for butanol dehydration.

5.6.1 Study of cellulose contribution

The cellulose (C-6288 Sigma) from Sigma Aldrich was used in this work. Experiments were carried out at the pre-determined optimum operating conditions that are 111°C, 135 kPa, 55 v/v% Bu-OH, and 3 mL/min. The particle size distribution of the cellulose was determined by

the particle size analyzer. The generated volume-based particle size distributions are shown in Fig. 5.13. The results showed that 75 vol% of particle sizes are within the range of 0.015-0.088 mm, 18% of particles are larger than 0.088 mm and only 7% of particles are smaller than 0.015 mm. The median of the size is 0.05 mm. The sizes of the cellulose particles are much smaller than that of CM. Because it is difficult to obtain the sizes of commercial cellulose same as that of the cellulose in the CM, the cellulose material used here are only considered to approximate the performance of butanol dehydration of actual cellulose in CM.

The butanol and water breakthrough curves obtained are shown in Fig 5.14 (a-b). As can be seen from butanol breakthrough curve in Fig.5.14a), the cellulose was able to remove water from butanol and produce over 93 v/v% butanol with a water adsorption capacity of 0.29 g/g-ads and water selectivity of 4.8 which were lower than that of CM at the same operation conditions, being 0.48 g/g-ads, and 5.4 respectively. The data are shown in Table 5.9.

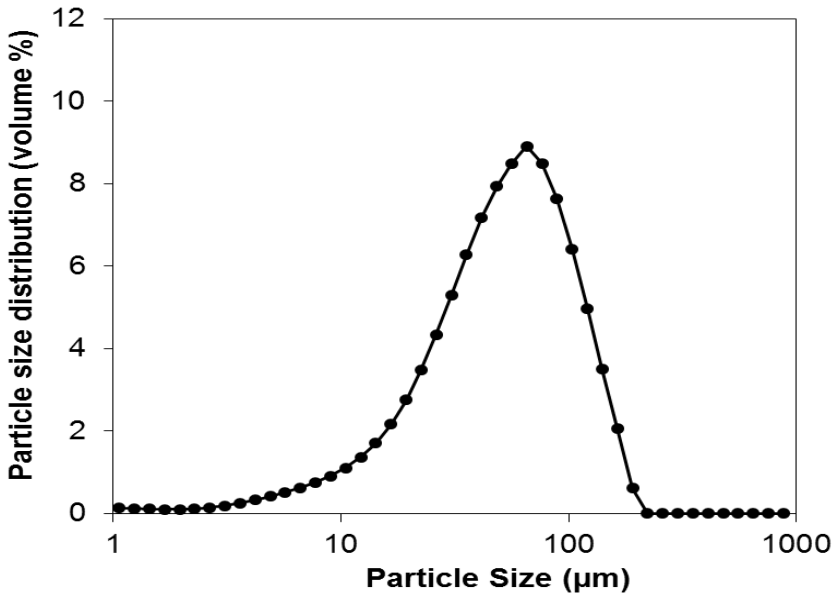
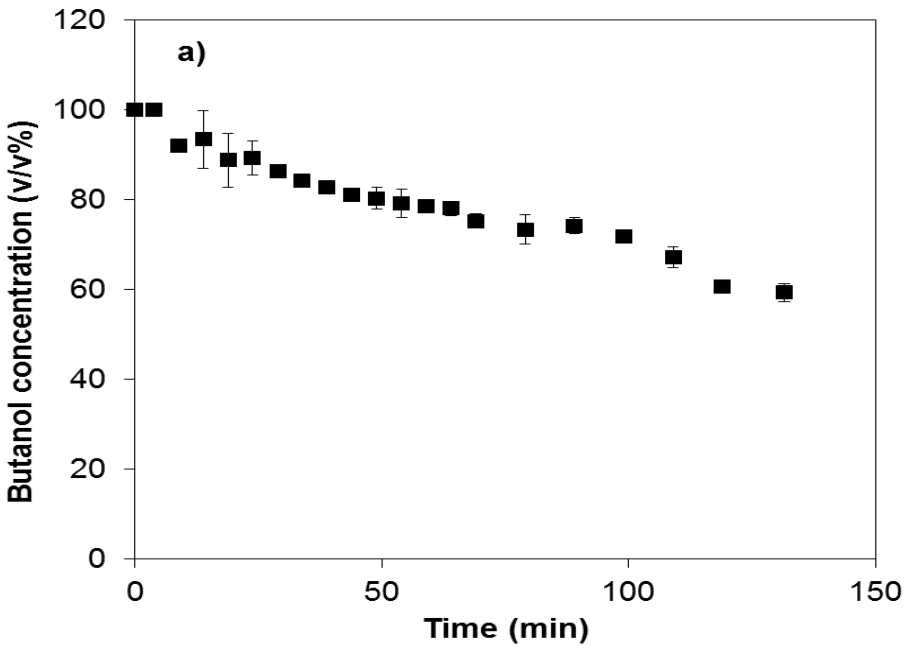


Figure 5.13 Particle size analysis of cellulose fraction

On the other hand, butanol uptake was much lower being 0.07 g/g-ads, similar to that of CM at 0.09 g/g-ads. The achieved maximum equilibrium water uptake of cellulose 0.29 g/g-ads in this work is similar to that reported for oak chips, and kenaf core being 0.28 g/g-ads, and 0.20 g/g-ads, respectively (Benson and George, 2005). In addition, it is much higher than that of the type 3A molecular sieves at 0.18-0.25 g /g-ads (Simo, 2008) which is most often used in industrial ethanol dehydration process.



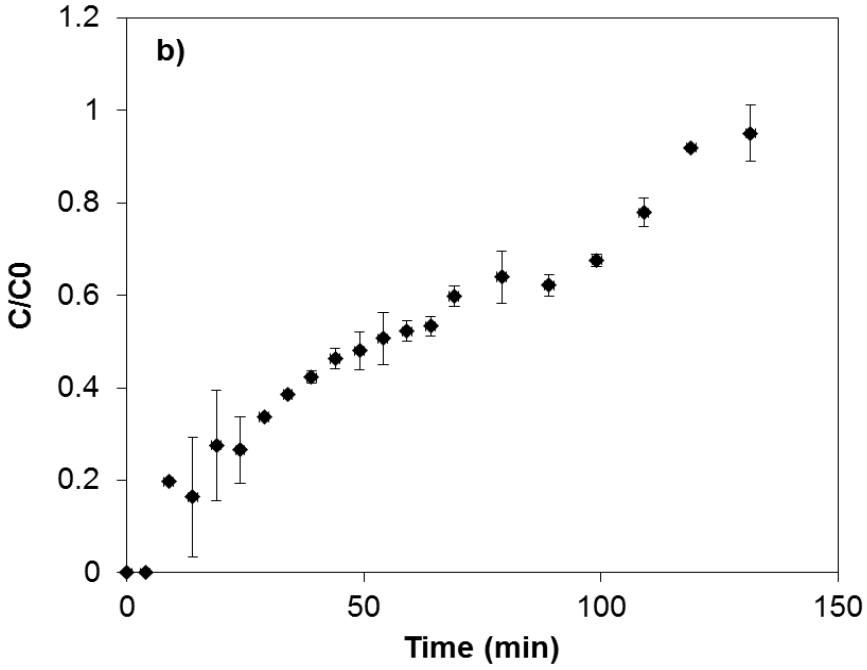


Figure 5.14 Breakthrough curves for cellulose fraction (a) Butanol concentration in the effluent (v/v%) vs. time. (b) Dimensionless water concentration in the effluent C/C0 vs. time

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3mL/min and particle size of cellulose fraction in the range of 0.015-0.088 mm

As shown in Fig.5.14 b, the water breakthrough curve exhibits a relatively sharp slope to reach equilibrium, indicating faster mass transfer rate because of it smaller particle sizes.

During the adsorption process, it was observed that the bed temperature initially increased, then went down when adsorption reach equilibrium as shown in Fig.5.15. It indicated that the adsorption is exothermic in nature. It is consistent with that observed for CM.

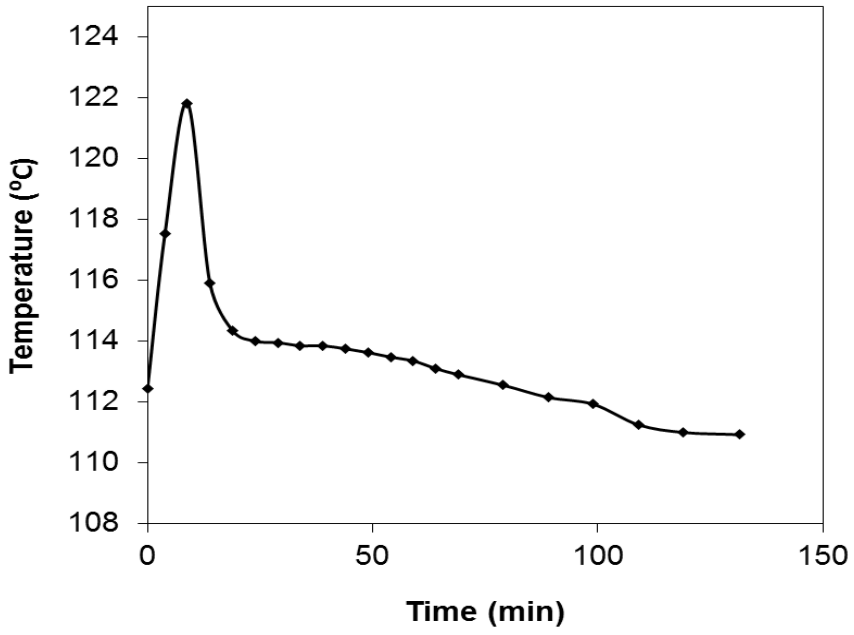


Figure 5.15 Average bed temperature profile during adsorption using cellulose as biosorbent in PSA

Experimental condition: All runs were at a temperature of 111°C, pressure of 201 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3mL/min and particle size of cellulose fraction in the range of 0.015-0.088 mm

The cellulose after saturation was regenerated at a temperature of 110°C by applying vacuum of 33 kPa with nitrogen purging from the bottom of the column at 850 mL min^{-1} for 5.5 h, same conditions as that for CM generation. Fig.5.16 shows that the cellulose was reused, and the butanol breakthrough curve of the regenerated cellulose is overlapped with that of the fresh one. That shows that the material is regenerable and reusable without any deterioration in its water adsorption capacity.

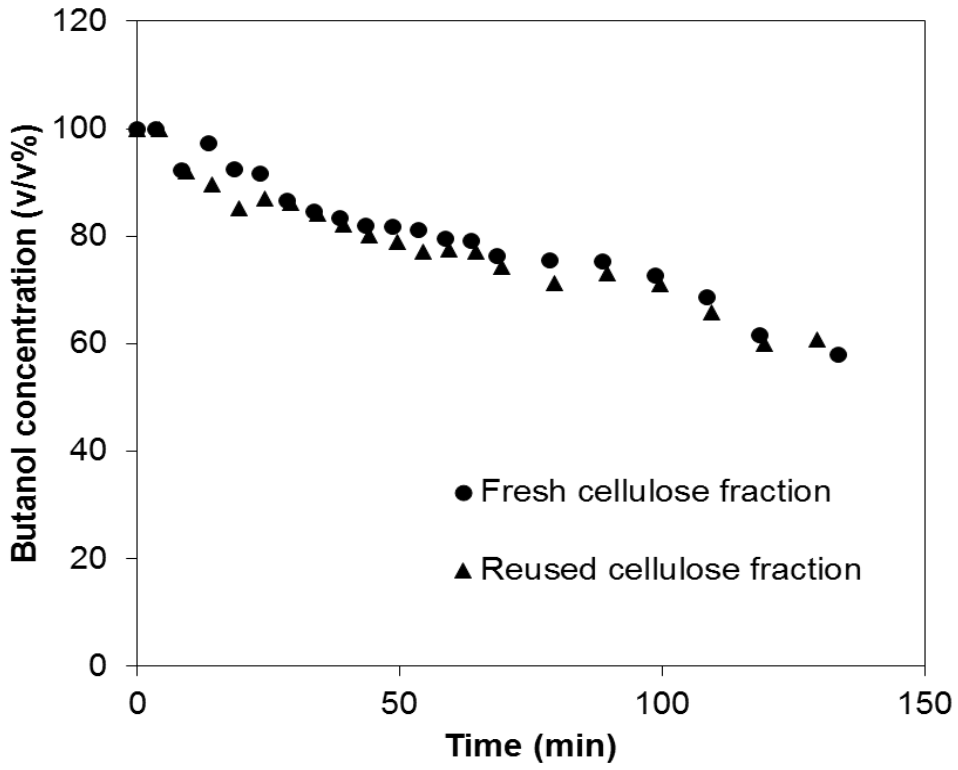


Figure 5.16 Butanol breakthrough curves to evaluate reusability for cellulose fraction

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55 v/v %, feed flow rate of 3mL/min and particle size of cellulose fraction in the range of 0.015-0.088 mm

An interesting observation in this work is that the water uptake and water selectively of cellulose is inferior to that of the CM material though the cellulose has smaller particle sizes. The results may indicate that physical structure of CM and its natural components may have a synergetic effect on selective water adsorption from butanol solution. However, it needs to be investigated further.

5.6.2 Study of protein fraction contribution

Protein-water interactions have been expressed by varying terminologies like water retention, water binding, water imbibing, water adsorption, and so on (Zayas, 1997). Water retention or the amount of water adsorbed by wet/dry form of protein is one of the important hydration properties of protein that marks its role in food applications. Although water binding can depend on composition and conformation of protein molecules, it also exhibits the swelling behavior due to spontaneous water uptake by protein matrix like that of starch molecules.

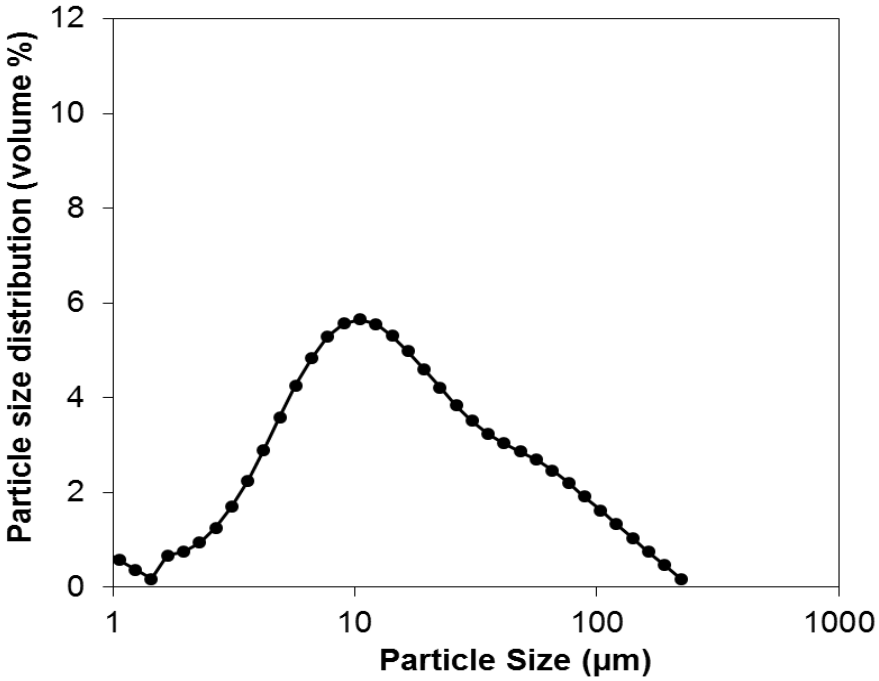
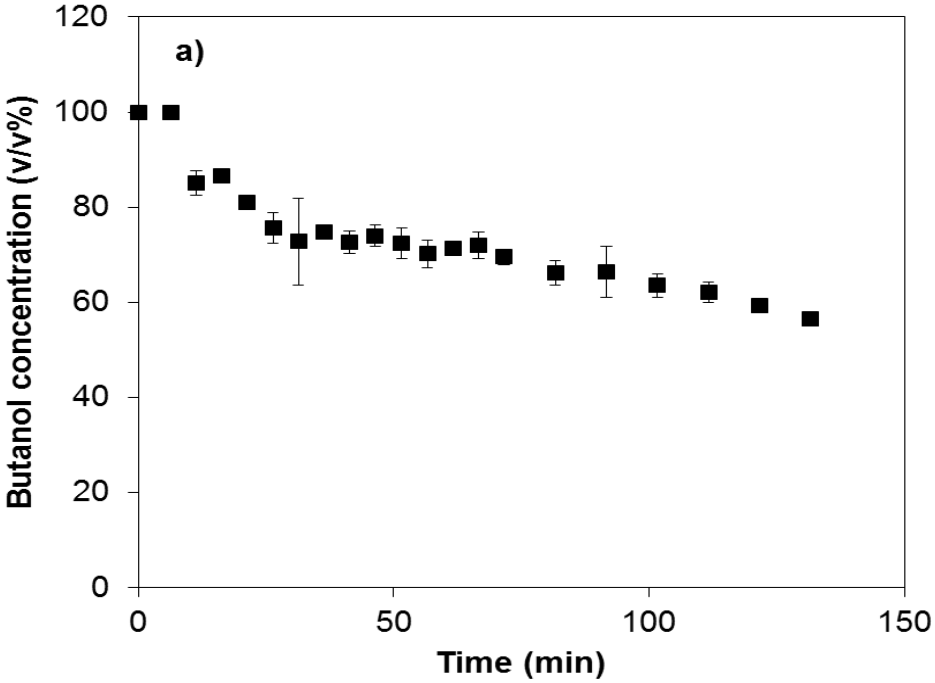


Figure 5.17 Particle size analysis of protein fraction

The experiments of butanol dehydration using protein were also carried out at the pre-determined optimum operating conditions that is 111°C, 135 kPa, 55 v/v% Bu-OH, and 3mL/min. Again, the particle size distribution generated by the particle size analyzer are shown

in Fig. 5.17. The results showed that 32 vol% of particle sizes are within the range of 0.02-0.12 mm, 64% are smaller than 0.02 mm and only 2% larger than 0.12 mm. The median of the size is 0.02 mm. The sizes are smaller than that of the cellulose, and CM used in this work.



From the butanol concentration profile in Fig.5.18a, it shows that the protein was able to concentrate butanol from 55% and achieved 85 v/v% which is lower than that of the cellulose material (97 v/v%) and CM (99.2 v/v%) . It also resulted in a lower water uptake of 0.20g/g-ads and a similar butanol uptake of 0.07g/g-ads as compared with the cellulose and CM. The lower butanol uptake might be because of the less accessible structure of the protein material and the interference of the protein hydrophobic regions with adsorption of polar water and butanol molecules. This result is consistent with the study carried out by Ostroff et al., (1998) wherein they showed that the whey proteins were able to adsorb water to some extent due to the presence of hydrophilic polar groups while its affinity for ethanol is less (Ostroff et al., 1988).

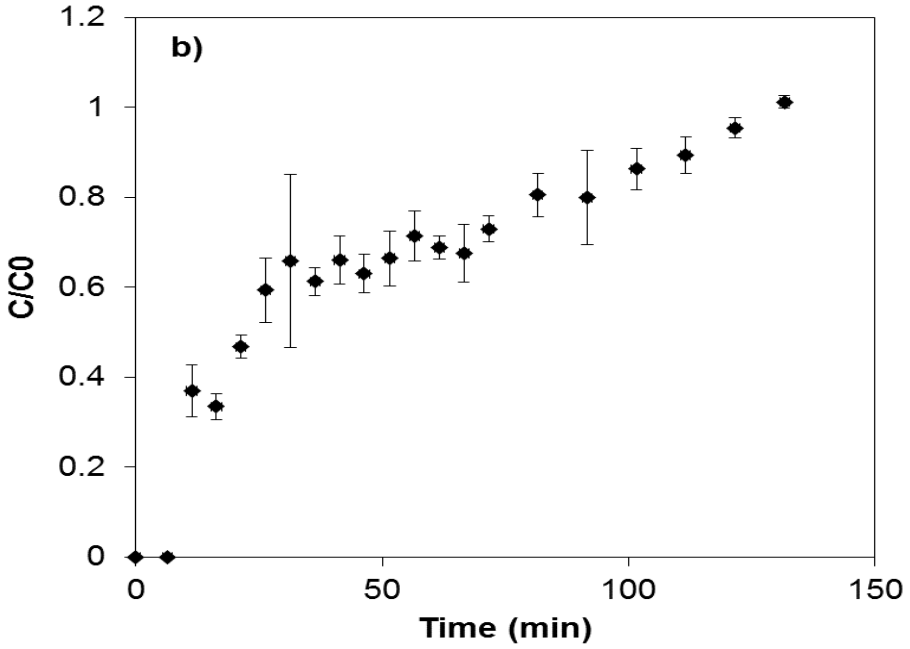


Figure 5.18 Breakthrough curves for protein fraction (a) Butanol concentration in the effluent (v/v%) vs. time. (b) Dimensionless water concentration in the effluent C/C0 vs. time

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55 v/v%, feed flow rate of 3mL/min and particle size of protein fraction in the range of 0.02-0.12 mm

In one of the studies by Hong et al. (1982), protein in the form of bovine serum albumin (BSA) was examined for the water adsorption capability from water-ethanol mixture as protein along with starch and xylan is one of the three major components of corn meal. They demonstrated similar results of protein with little to no capacity to adsorb ethanol whereas it weakly adsorbed water as compared to other major ingredients- starch and xylan. It proved that protein had a less significant role in water adsorption properties of corn meal (Hong et al., 1982). During the adsorption process, again the bed temperature was increased showing that the adsorption is exothermic in nature as shown in Fig.5.19.

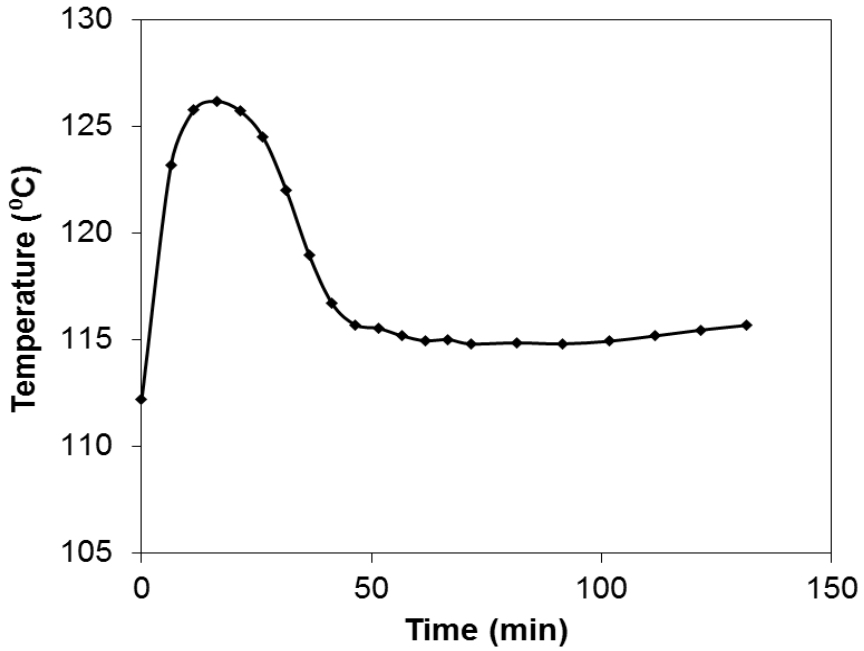


Figure 5.19 Average bed temperature profile during adsorption using protein fraction as biosorbent in PSA

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55 v/v%, feed flow rate of 3mL/min and particle size of protein fraction in the range of 0.02-0.12 mm

Protein after use as adsorbent for butanol dehydration was also regenerated at a temperature of 110°C by applying vacuum of 33 kPa with nitrogen purging from the bottom of the column at 850 mL min^{-1} for 5.5 h, same conditions as that for cellulose regeneration. Fig.5.20 shows that the regenerated protein was still able to concentrate butanol from 55 v/v% to over 85 v/v%, similar to the fresh material. It shows that the protein is regenerable and reusable without any deterioration in its water adsorption capacity.

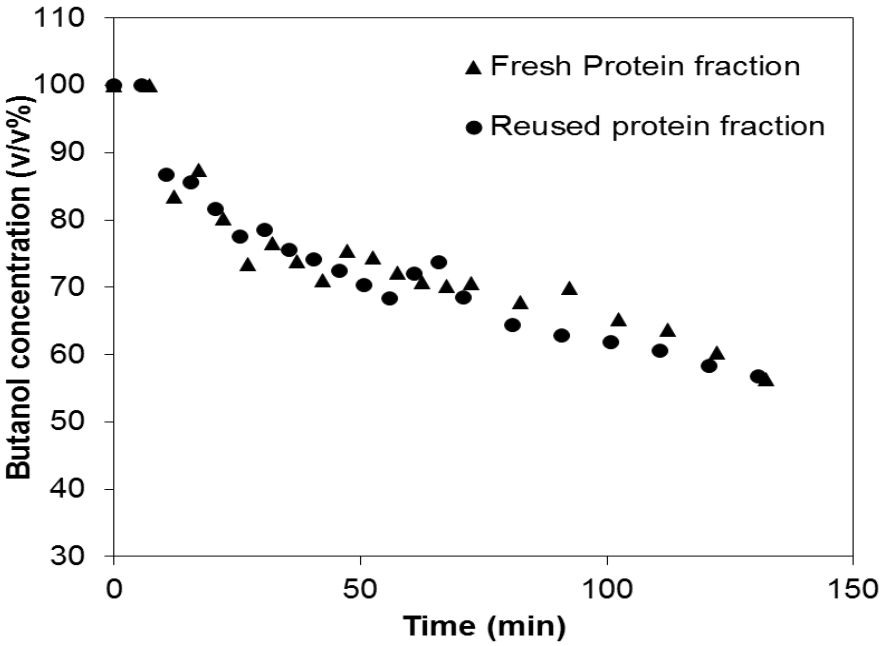


Figure 5.20 Butanol breakthrough curves to evaluate reusability for protein fraction

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55 v/v%, feed flow rate of 3mL/min and particle size of protein fraction in the range of 0.02-0.12 mm

Butanol recovery and maximum achievable butanol concentration using protein was on the lower end. A recovery of only 82% and a maximum butanol concentration of 85 v/v% were obtained with a lower water equilibrium selectivity of 2.8. The results obtained from this experiments demonstrated that protein is not an effective component for selective water uptake. Table 5.9 summarizes the water uptake, butanol uptake and water selectivity of the cellulose, and protein fractions along with CM, so as to enable a clear comparison and understanding of the component fractions' contributions to water adsorption capacity of CM.

Table 5.9 Results from the study of fraction contributions

Adsorbents	Water uptake (g/g-ads)	Butanol uptake (g/g-ads)	Equilibrium Water selectivity	Butanol recovery (%)	Max. Effluent butanol concentration achieved (v/v %)
Cellulose fraction	0.29 ± 0.03	0.07 ± 0.02	4.27 ± 1.04	84.36 ± 1.26	93.43 ± 1.31
Protein fraction	0.20 ± 0.00	0.08 ± 0.00	2.79 ± 0.17	82.47 ± 1.06	84.56 ± 0.64
CM	0.48 ± 0.02	0.09 ± 0.00	5.43 ± 0.08	90.11 ± 0.26	99.20 ±0.79

* g adsorbed/ g dry net weight of adsorbent at equilibrium conditions

It can be found that the water uptake and selectivity from the cellulose are much higher than those from protein, affirming that cellulose plays a more important role in the butanol dehydration. However, the performance of pure cellulose is not as effective as that of the CM material. Other components in CM, or physical structure of CM may attribute to the high water uptake. Further investigations are required in this regard.

5.7 Capabilities of other biosorbents for butanol dehydration

5.7.1 Butanol dehydration using corn meal

Corn meal, a representative of starchy material is studied so as to compare the performance of starchy corn meal with cellulosic canola meal on butanol dehydration in a PSA process. Corn meal that was used for experiments was a product of Purity Inc, a trademark company of ADM Agri-Food Company Ltd. Like cellulosic materials, starch and starch-based adsorbents were reported to selectively dehydrate alcohols especially because of their affinity to water (Ladisch et al., 1979; Ladisch et al., 1984; Westgate and Ladisch, 1993) . Corn meal which is a good source of starch has been demonstrated to adsorb water from ethanol by many studies (Chang et al., 2006b; Hong et al., 1982; Ladisch et al., 1984). The ability of starch to selectively

adsorb water is a result of interaction in the form of hydrogen bonding between free hydroxyl groups (-OH) on their glucose units and the water molecules (Boonfung and Rattanaphanee, 2010) and alternatively by capillary action (Sun et al., 2013).

The experiments were carried out at the optimum operating conditions proposed for CM that are 111°C, 135 kPa, 55 v/v% Bu-OH, and 3mL/min. The volume-based particle size distributions are shown in Fig. 5.21. The results show that 92 vol% of particle sizes are within the range of 0.2-1.19 mm, 5% are larger than 1.19 mm and only 2% are smaller than 0.2 mm. The median of the size is 0.75 mm.

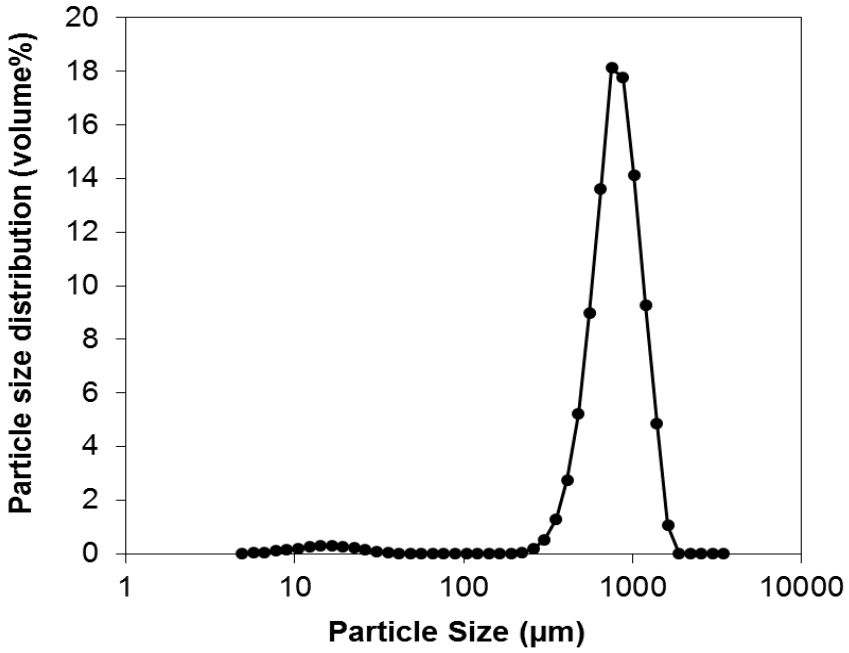


Figure 5.21 Particle size analysis of corn meal

From the breakthrough profiles of water and butanol shown in Fig.5.22 a-b), it's found that corn meal was able to concentrate butanol from 55 v/v% and produce 98 v/v% butanol with a water adsorption capacity of 0.18 g/ g-ads as shown in Table 5.10. This water adsorption capacity was seen to be coherent with the one reported by a study made on corn starch for

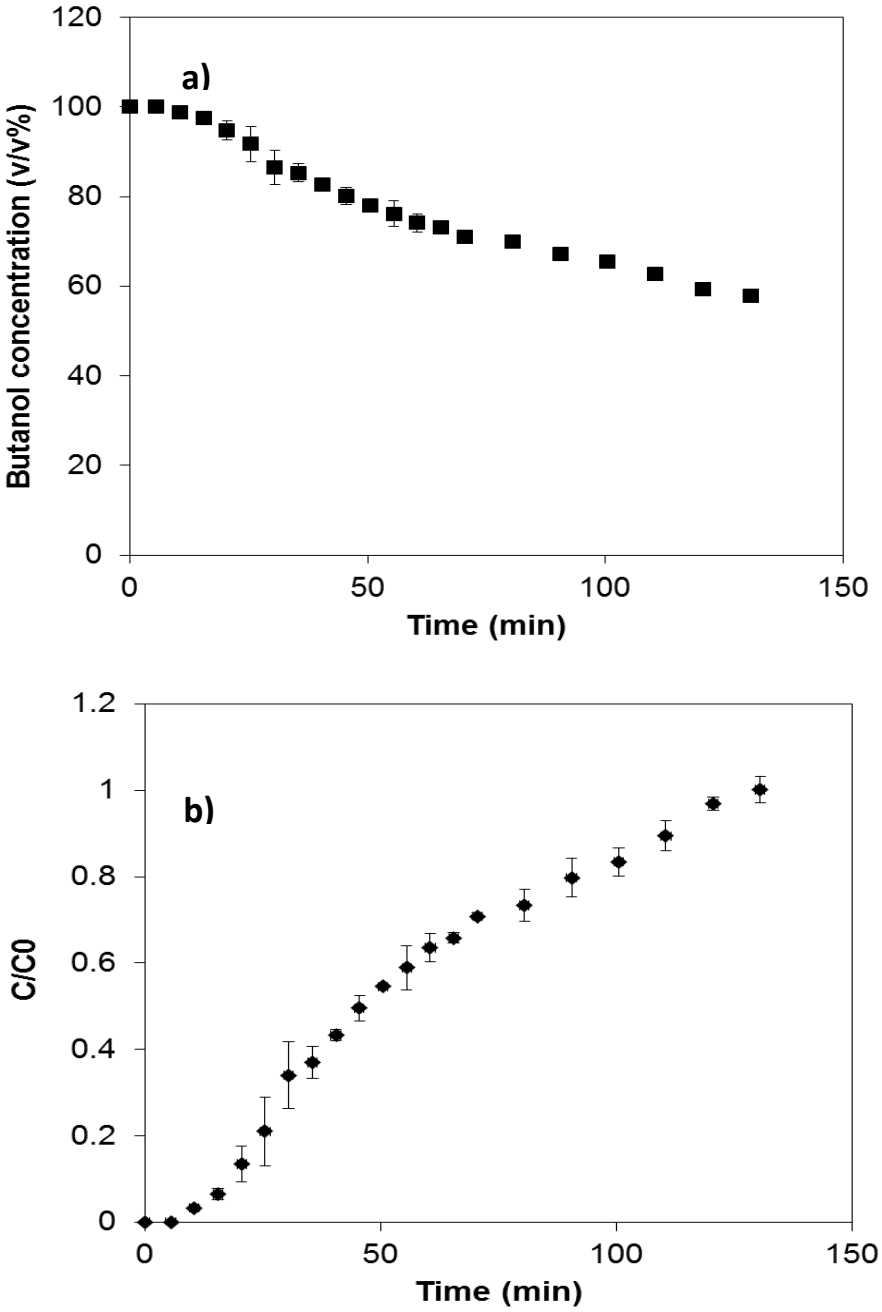


Figure 5.22 Breakthrough curves for corn meal (a) Butanol concentration in the effluent (v/v%) vs. time. (b) Dimensionless water concentration in the effluent C/C0 vs. time

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55v/v %, feed flow rate of 3mL/min and particle size of corn meal in the range of 0.2-1.19 mm

ethanol dehydration where it had a water uptake of 0.19 g/g-ads (Quintero and Cardona, 2009). However, it is lower than that of CM in this work (0.48 g/g-ads). It was reported (Hong et al., 1982) that in general, starchy materials have higher water uptake than cellulosic materials.

The fact that the water binds more strongly to amylopectin due to its branched chain nature, which makes the starch material to have higher water uptake than cellulose (Vareli et al., 2000), however the diffusing water molecules cause mechanical strain that results in an unexplored swelling behavior of starch (Westgate and Ladisch, 1993) while cellulose materials have a stable structure even after water adsorption (Westgate and Ladisch, 1993; Witono et al., 2014).

However, CM containing cellulose in this work has higher water uptake than starchy corn meal, and is stable for multiple reuse. CM has multi-components such as protein, cellulose, hemicellulose, lignin, etc. A synergetic effect of these components and physical properties of CM make it a promising material for butanol dehydration in terms of high water uptake, and stability.

The amount of butanol adsorbed on corn meal at equilibrium is about 0.04g-g-ads showing that only a small amount of butanol is adsorbed. However, because the corn meal's water uptake is lower than that of CM, the equilibrium water selectivity over butanol was 4.79, which was also lower than that of CM, 5.4.

During the adsorption process, bed temperature was observed to be increased, which then went down when adsorption reached equilibrium as shown in Fig.5.23. This indicated that the adsorption is exothermic in nature.

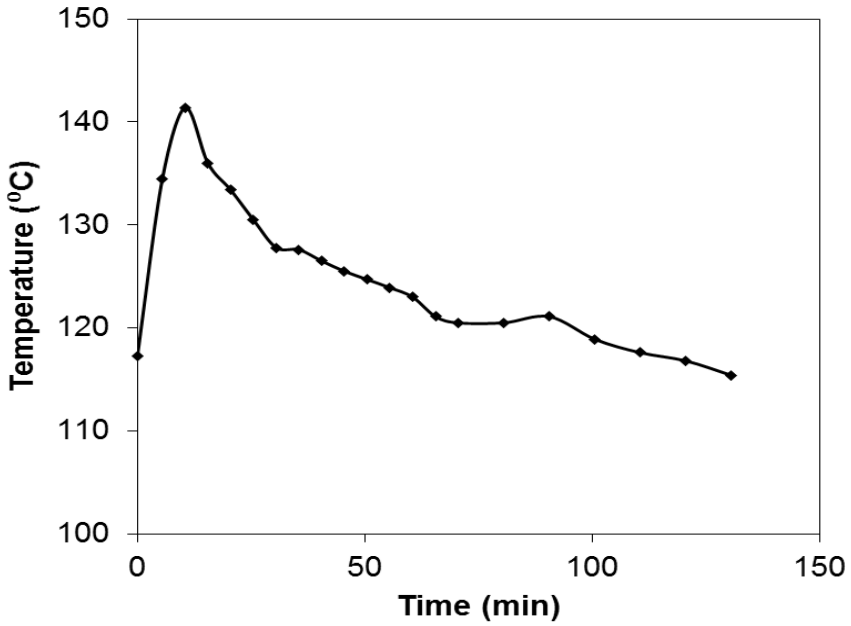


Figure 5.23 Average bed temperature profile during adsorption using corn meal as biosorbent in PSA

Experimental condition: All runs were at a temperature of 111°C, pressure of 135 kPa, butanol feed concentration of 55v/v %, feed flow rate of 3mL/min and particle size of corn meal in the range of 0.2-1.19 mm

Table 5.10 summarizes the data. Although corn meal had proven to perform better for water adsorption for ethanol-water mixtures (Chang et al., 2006a; Chang et al., 2006b; Ladisch et al., 1984), it seems that it has neither displayed a higher water uptake nor water selectivity within the tested range of conditions.

Table 5.10 Comparison of water and butanol uptakes by corn meal with canola meal

Adsorbents	Water uptake *	Butanol uptake *	Equilibrium water selectivity	Butanol recovery (%)	Max. Effluent butanol concentration achieved (v/v %)
Corn meal	0.18 ± 0.00	0.04 ± 0.00	4.79 ± 0.23	87.76 ± 0.81	98.44 ± 0.27
CM	0.48 ± 0.02	0.09 ± 0.00	5.43 ± 0.08	90.11 ± 0.26	99.20 ±0.79

* g adsorbed/ g dry net weight of adsorbent at equilibrium conditions

In 2011, average per capita consumption of Canadians was 0.52 kg of corn meal and flour, and corn meal is also used indirectly to feed livestock (Statistics Canada, 2014b). Considering the ongoing debate of food vs fuel, use of corn meal could be avoided to due to its use as a form of staple food for both humans and livestock.

5.7.2 Butanol dehydration using oat hulls

Oat hulls, for this study was obtained from Richardson Millings Ltd, Warman, SK, Canada. From the analytical report of OH given by Richardson Millings Ltd through the lab analysis at SGS Agri-Food Laboratories, Guelph, ON, it was found to contain over 46% of fiber content. Notably, it also contains almost 34% starch in it, which is due to the presence of residual starch post-milling process. The efficiency of milling or starch extraction is out of scope of this work. However, high content of starch, cellulose and hemicellulose is desirable in biomass as these groups are responsible for water adsorption (Okewale et al., 2013).

The preliminary experiments were carried out to examine the performance of oat hull on butanol dehydration at the following conditions: temperature of 100^{o}C, pressure of 135 kPa, feed butanol concentration of 68 v/v%, feed flow rate of 3 mL min^{-1} and adsorbent particles size of 0.425-1.18 mm. The size analyzer generated the results as volume-based particle size distributions as shown in Fig. 5.24. The results showed that 71 vol% of particle sizes are within the range of 0.42-1.19 mm, 31% are 23% are smaller than 0.42 mm and only 5% are bigger than 1.19 mm. The median of the size is 0.6 mm.

The butanol and water breakthrough curves are presented in Fig. 5.25 a) and b). From the resultant butanol production profiles and water breakthrough curves in those tested ranges of values, oat hulls successfully concentrated butanol to >97 v/v% from an initial feed solution

containing 68 v/v% butanol with a water adsorption capacity of 0.33 g g-ads^{-1}. This demonstrated that oat hulls were able to concentrate butanol by selective removal of water, demonstrating great potential for application in butanol dehydration.

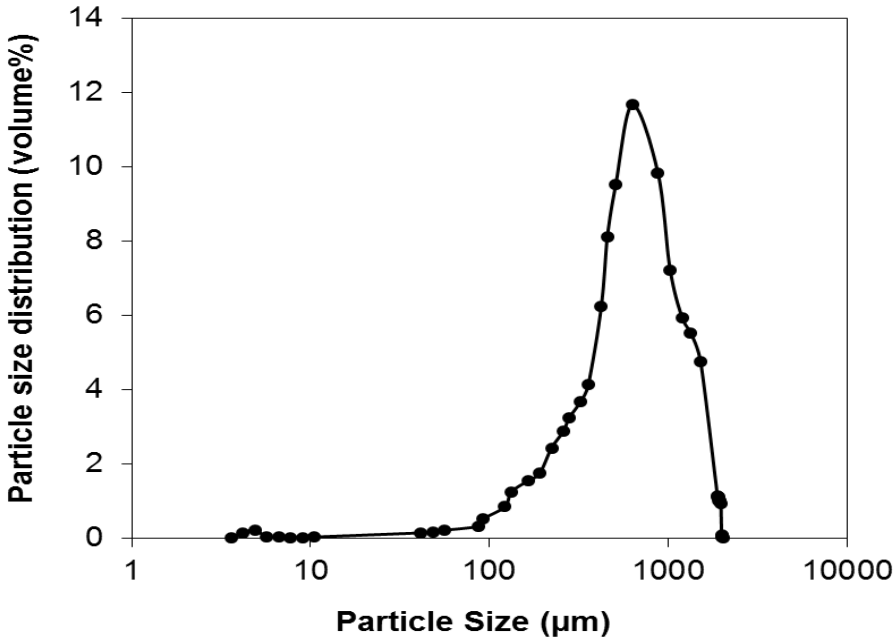


Figure 5.24 Particle size analysis of oat hulls

The equilibrium water selectivity over butanol was found to be 1.65 for CM and the amounts of water and butanol adsorbed at the equilibrium were 0.33 g g-ads^{-1} and 0.27 g g-ads^{-1} for OH, respectively.

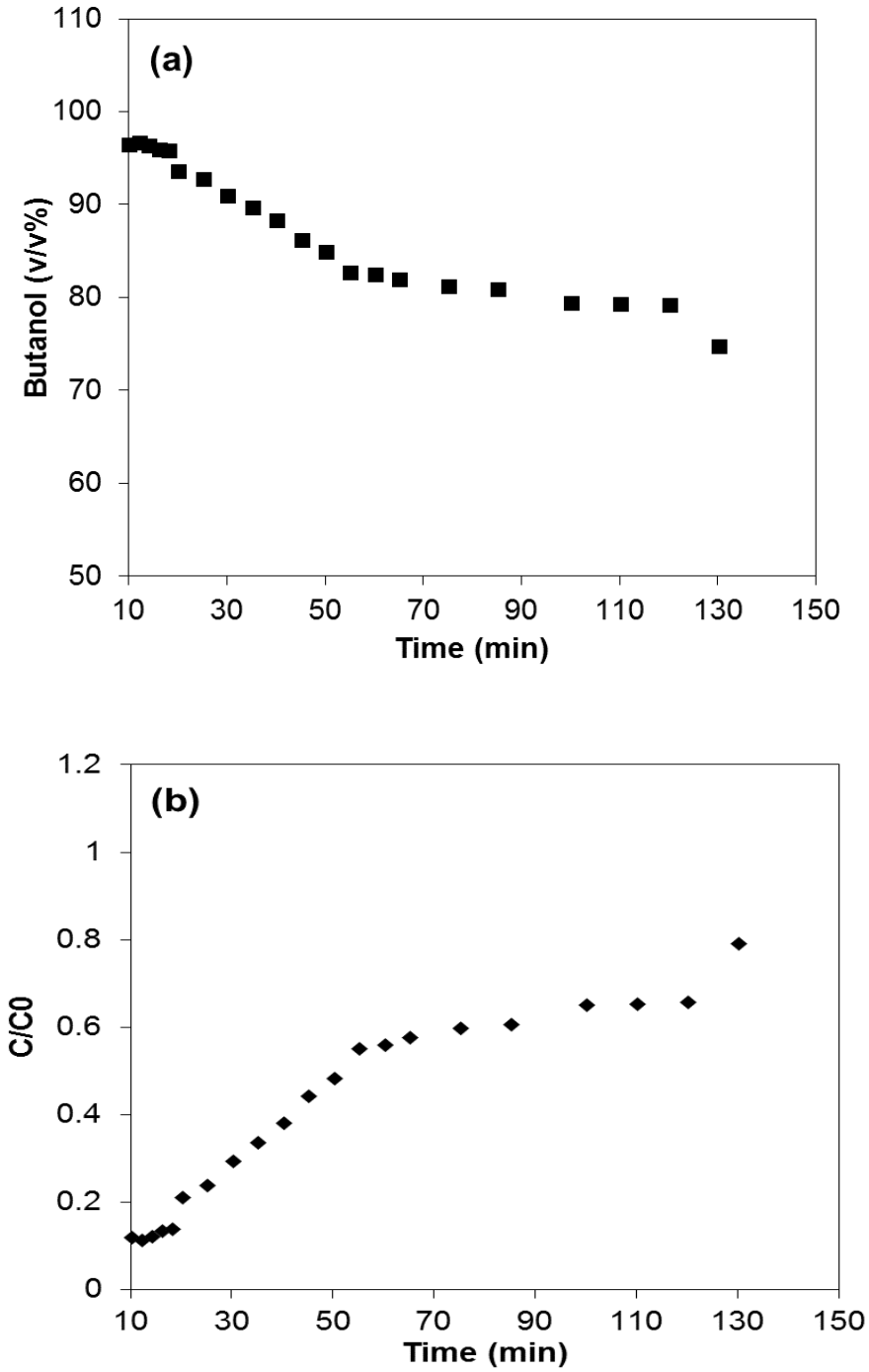


Figure 5.25 Breakthrough curves for oat hulls (a) Butanol concentration in the effluent (v/v%) vs. time. (b) Dimensionless water concentration in the effluent C/C0 vs. time

Experimental condition: All runs were at a temperature of 100°C, pressure of 135 kPa, butanol feed concentration of 68 v/v%, feed flow rate of 3mL/min and particle size of oat hulls in the sieved range of 0.42-1.19 mm

Heat was generated during the course of adsorption process due to which bed temperature was observed to be increased as shown in Fig.5.26. This again confirms that the adsorption is exothermic in nature.

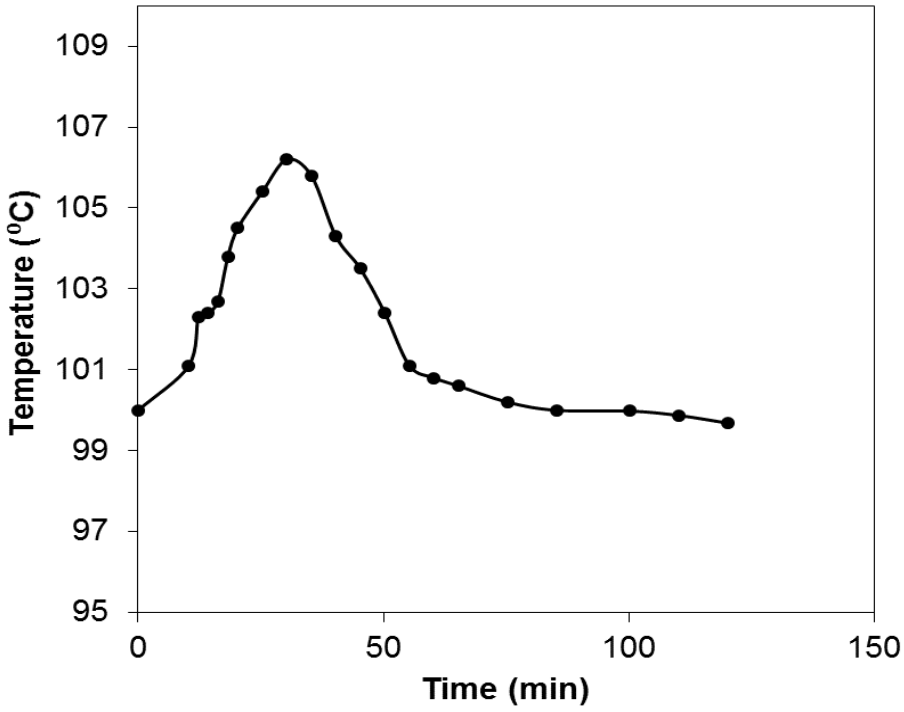


Figure 5.26 Average bed temperature profile during adsorption using oat hulls as biosorbent in PSA

Experimental condition: All runs were at a temperature of 100°C, pressure of 135 kPa, butanol feed concentration of 68 v/v%, feed flow rate of 3mL/min and particle size of oat hulls in the sieved range of 0.42-1.19 mm

OH residue from oat industry has an abundance of hydroxyl groups from their molecular makeup due to the presence of cellulose, hemicellulose, lignin and starch that are instrumental in the adherence water molecules to the surface of the adsorbent. A more detailed and systematic investigation of oat hull on butanol dehydration is recommended to be done in order to develop biosorbents based oat hull.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The adsorption capability of CM for butanol dehydration was investigated in a bench-scale pressure swing adsorption system. The equilibrium and kinetic studies of the process was carried out through breakthrough experiments and the experiments proved that CM has the ability to adsorb water and dehydrate butanol to achieve fuel grade product. Water saturated CM was regenerated by at 110°C under vacuum and reused without any deterioration in adsorbent capability and quality.

Further experiments were designed as per OAD design tool and optimum operating conditions were found for butanol dehydration. It was demonstrated that biosorbents based on CM has the capability to dry butanol from the azeotropic butanol concentration of 55 v/v% to achieve high purity butanol of 99 v/v%.

Pressure was found to be the most significant factor, affecting butanol uptake, water selectivity, butanol recovery, and maximum effluent butanol concentration, whereas butanol feed concentration was the second most significant affecting water uptake. The lower the pressure, the lower the butanol uptake and the higher the water selectivity, butanol recovery, and maximum effluent butanol concentration. The validation experiments carried out at the optimum conditions proposed from the range analysis of the OAD method resulted in a water selectivity of 5.4, butanol recovery of 90%, water uptake of 0.48 g g-ads^{-1} and fuel grade butanol of over 99 v/v% which are better than that obtained at any other conditions in this work. The effect of particle size on butanol dehydration within the tested range was demonstrated to have insignificant effect on

adsorption and mass transfer rate. The water uptake values were 0.48 g/g-ads and 0.47 g/g-ads with CM particles of 0.425-1.18mm and 4.7mm respectively; with both particle sizes, butanol recovery of 90% and maximum butanol effluent concentration of 99 v/v% were achieved. Similar results obtained is thus evident of negligible particle size effects in the tested range.

The equilibrium study was conducted using the breakthrough curves and it was demonstrated that the Dubinin- Polanyi model based on the adsorption potential theory for large pore materials gave a better fit to the water adsorption isotherms. The mean energy determined by the Dubinin-Polanyi model indicated that water adsorption is physisorption in nature. The heat of the water adsorption was estimated to be -28.9 kJ/ mol, indicating an exothermic nature. Furthermore, the Gibb's free energy ΔG° determined for water adsorption in this work affirm that the water adsorption process is spontaneous.

Study of fraction contributions in CM towards adsorption capacity showed that the cellulose fraction plays a more important role in the water uptake than the protein fraction. Moreover, when a starchy material like corn meal was investigated for water adsorption capacity for butanol dehydration in the same range of newly found optimum conditions, it was found that CM performed better in terms of water uptake and selectivity than corn meal. CM showed a water uptake of 0.48 g/g-ads and selectivity of 5.43 while corn meal showed values of 0.18 g/g-ads and 4.8 respectively. A preliminary study on cellulosic material like OH also showed strong potential to dehydrate butanol and hence this material could be a promising biosorbent for drying butanol which needs further systematic investigation.

6.2 Recommendations

1) Selectivity of CM can further be improved by any pre-treatment with acid or combination with other materials.
2) The effect of butanol adsorption could be considered in the adsorption isotherm model to make more accurate justifications.
3) Mathematical modeling could be evaluated to predict the breakthrough curves.
4) CM used in this study has a significant amount of protein left. Improving protein extraction could help decrease the amount of protein in the canola meal.
5) PSA system deployed could be modified so as to decrease the extent of butanol loss after exiting the bed in the condenser; the regeneration part of the bed could also be enhanced to make adsorbate measurements possible.
6) Online measurement could be incorporated into the system to measure water and the effluent butanol leading to much accurate results.

7 REFERENCES

Agri-Food Canada, "Oats: Situation and Outlook," Agriculture and Agri-Food Canada. (2013).

Aider, M. and C. Barbana, "Canola proteins: composition, extraction, functional properties, bioactivity, applications as a food ingredient and allergenicity- A practical and critical review," Trends in Food. Sci. Technol. **22**, 21-39 (2011).

Al-Asheh, S., F. Banat and N. Al-Lagtah, "Separation of Ethanol-Water Mixtures using Molecular Sieves and Biobased Adsorbents," Chem. Eng. Res. Des. **82**, 855-864 (2004).

Anozie, A.N., E.E. Okuhon, F.N. Osuolale and J.K. Adewole, "Dehydration of Ethanol-Water Mixture Uisng Activated Carbons from Sawdust and Palm Kernel Shells," Sep. Sci. Technol. **45**, 1482-1489 (2010).

Babu, V., A. Thapliyal and G. Patel Kumar, "Biofuels Production," John Wiley & Sons, India (2013), pp. 392.

BASF, "Petrochemicals- n-Butanol," CP Petrochemicals Division, BASF, Europe. **1**, 3 (2008).

Baylak, T., P. Kumar, H.C. Niu and A. Dalai, "Ethanol Dehydration in a Fixed Bed Using Canola Meal," Energ. Fuels. **26**, 5226-5231 (2012).

Beery, K.E. and M.R. Ladisch, "Chemistry and properties of starch based dessicants," Enzyme. Microb. Technol. **28**, 573-581 (2001).

Benson, T.J. and C.E. George, "Cellulose based adsorbent materials for the dehydration of ethanol using thermal swing adsorption," Adsorpt. **11**, 697-701 (2005).

Biagini, E., F. Barontini and L. Tognotti, "Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique," Ind. Eng. Chem. Res. **45**, 4486-4493 (2006).

Bobok, D. and Besedova.E, "Mechanism of Ethanol Vapors Diffusion in Particles of Activated Carbon," Chem. Paper. **58**, 55-63 (2003).

Boonfung, C. and P. Rattanaphanee, "Pressure Swing Adsorption with Cassava Adsorbent for Dehydration of Ethanol Vapor," World. Acad. Sci. Eng. and Technol. **4**, 557-560 (2010).

Canola Council of Canada, "Current Canola Oil, Meal, and Seed prices," **2014**.

Chang, H., X. Yuan, H. Tian and A. Zeng, "Experimental Investigation and Modeling of Adsorption of Water and Ethanol on Cornmeal in an Ethanol-Water Binary Vapor System," Chem. Eng. Technol. **29**, 454-461 (2006a).

Chang, H., X. Yuan, H. Tian and A. Zeng, "Experimental Study on the Adsorption of Water and Ethanol by Cornmeal for Ethanol Dehydration," Ind. Eng. Chem. Res. **45**, 3916-3921 (2006b).

Chao, J., Y. Mingfa, H. Liu, F.L. Chia-fon and J. Jing, "Progress in the production and application of n-butanol as a biofuel," Renew. Sust. Energ. Rev. **15**, 4080-4106 (2011).

Crini, G. and M. Badot, Eds., "Sorption processes and pollution: Conventional and non-conventional sorbents for pollutant removal from wastemaster," Presses Univ. Franche-Comté, France (2010), pp. 490.

Dada, A.O., A.P. Olalekan, A.M. Olantunya and O. Dada, "Langmuir, Freundlich,Temkin , and Dubinin-Radushkevich Isotherm Studies of Equilibrium Sorption of Zn2+ Unto Phosphoric Acid Modified Rice Husk," J. Appl. Chem. **3**, 38-45 (2012).

Dang, V.B.H., H. Doan D, T. Dang-Vu and A. Lohi, "Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw," Bioresource Technol. **100**, 211-219 (2009).

El Haddad, M., "Kinetic and Thermodynamic studies on the adsorption behavior of Rhodamine B dye onto animal bone meal," J. Chem. Eng. Mat. Sci. **3**, 38-44 (2012).

Gismatullin, E. and K. Lundgren, "Branson's Butanol Heading to U.S. as Ethanol Substitute," Bloomberg. Com. **2014**.

Gupta Kumar, V., M. Schmoll, M. Makki, M. Tuohy and M. Mazutti Antonio, Eds., "Applications of Microbial Engineering," CRC Press, Austria (2013), pp. 504.

Hamel, M. and E. Dorff, "Corn: Canada's third most valuable crop," Statistics Canada., 1 (2015).

Harper, J., O. Haroer, S. Mayhew, M. Nightlinger and S. Ormsby, "The World's Diminishing Oil," The League of Women Voters of the Fairfax Area Education Fund. **EF-1**, 1 (2009).

Himmelsbach, S.D., S. Khalili and E.D. Akin, "The use of FT-IR microspectroscopic mapping to study the effect of enzymatic retting of flax (*Linum usitatissimum* L) stems," J. Sci. Food. Agri. **82**, 685 (2002).

Hong, J., M. Voloch, M.R. Ladisch and G.T. Tsao, "Adsorption of ethanol-water mixtures by biomass materials," Biotechnol. Bioeng. **24**, 725-730 (1982).

Khan, A.A. and R.P. Singh, "Adsorption thermodynamics of carbofuran on Sn(IV) arsenosilicate in H+, Na+ and Ca2+ forms, " J. Colloid. Sci. **24**, 33- 42 (1987).

Kumar, S., N. Singh and R. Prasad, "Anhydrous ethanol: A renewable source of energy," Renew. Sust. Energ. Rev. **14**, 1830-1844 (2010).

Ladisch, M.R. and K.K. Dyck, "Dehydration of ethanol: new approach gives positive energy balance," Sci. **205**, 898-900 (1979a).

Ladisch, M.R., M. Voloch, K.K. Dyck and J. Allen, "Energy Efficient Dehydration of Ethanol," Sci. 178th National Meeting of the American Chemical Society, Washington, DC (1979b).

Ladisch, M.R., M. Voloch, J. Hong, P. Blenkowski and G.T. Tsao, "Cornmeal Adsorber for Dehydrating Ethanol Vapors," Ind. Eng. Chem. Proc. DD. **23**, 437-443 (1984).

Ladisch, R.M., "Fermentation-derived butanol and scenarios for its uses in energy-related applications," Enzyme. Microb. Technol. **13**, 280-283 (1991).

Lee, Y.J., J.P. Westgate and R.M. Ladisch, "Water and Ethanol Sorption Phenomena on Starch," AIChE. **37**, 1187-1195 (1991).

Lin, X., J. Wu, J. Fan, W. Qian, X. Zhou, C. Qian, X. Jin, L. Wang, J. Bai and H. Ying, "Adsorption of butanol from aqueous solution onto a new type of macroporous adsorption resin: Studies of adsorption isotherms and kinetics simulation," J Chem Technol Biotechnol. **87**, 924-931 (2012a).

Lin, X., J. Wu, X. Jin, J. Fan, R. Li, Q. Wen, W. Qian, D. Liu, X. Chen, Y. Chen, J. Xie, J. Bai and H. Ying, "Selective separation of biobutanol from acetone-butanol-ethanol fermentation broth by means of sorption methodology based on a novel macroporous resin," Biotechnol. Prog. **28**, 962-972 (2012b).

Luyben, L.W., "Control of the Heterogeneous Azeotropic n-Butanol/Water Distillation system," Energ. Fuel. **22**, 4249-4258 (2008).

Medina, A.R., P.M. Gamero, J.M.R. Almanza, D.A.H. Cortes and G.G. Vargas, "Study of the zeolitization process of fly ash using an Orthogonal Array of Taguchi Experimental Design," J. Chil. Chem. Soc. **54**, 244-251 (2009).

Melzoch, K., P. Patakova, M. Linhova, J. Lipovsky, P. Fribert, M.S.S. Toure, M. Rychtera, M. Pospisil and G. Sebor, "Experiences in the production and use of butanol as biofuel," ICT Prague. (2010).

Meng, L., X. Zhang, Y. Tang, K. Su and J. Kong, "Hierarchially porous silicon-carbon-nitrogen hybrid materials towards highly efficient and selective adsorption of organic dyes," Sci. Rep. **5**, 7910-7923 (2015).

Moreira, A.R., D.C. Ulmer and J.C. Linden, "Butanol toxicity in butylic fermentation," Biotechnol. Bioengin,Symp. **11**, 567-579 (1981).

Namboodiri, V.V. and L.M. Vane, "High permeability membranes for the dehydration of low water content ethanol by pervaporation," J. Membr. Sci. **306**, 209-215 (2007).

Newkirk, R., "Canola Meal- Feed Industry Guide," Canola Council of Canada. 24 (2009).

Nigam, P. and A. Singh, "Production of liquid biofuels from renewable resources," Prog. Energ. Comb. Sci. **37**, 52-68 (2011).

Okewale, A.O., K.A. Babayemi and A.P. Olalekan, "Adsorption Isotherms and Kinetic Models of Starchy Adsorbents on Uptake of Water from Ethanol-Water Systems," Int. J. Appl. Sci. Technol. **3**, 35-42 (2013).

Ostroff, A., E. Hatzidimitriu and J.L. Kokini, "Thermodynamics of Water and Ethanol Adsorption on Model Biomass systems," Biotechnol. Bioeng. **31**, 880-884 (1988).

Ou, H., W. Tan, C. Niu Hui and R. Feng, "Enhancement of the Stability of Biosorbents for Metal-Ion Adsorption," Ind. Eng. Chem. Res. **54**, 6100-6107 (2015).

Polanyi, M., "Causes of Forces of Adsorption," Z Elektrochem. **26**, 370-374 (1920).

Quintero, A.J. and A.C. Cardona, "Ethanol Dehydration by Adsorption with Starchy and Cellulosic Materials," Ind. Eng. Chem. Res. **48**, 6783-6788 (2009).

Qureshi, N., S. Hughes, I.S. Maddox and M.A. Cotta, "Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption," Bioproc. Biosyst Engg. **27**, 215-222 (2005).

Qureshi, N. and H.P. Blaschek, "Butanol production from agricultural biomass." CRC Taylor and Francis, Oxford, U.K (2006), pp. 525-549.

Ramaswamy, S., J.H. Huang and V.B. Ramarao, Eds., "Separation and Purification Technologies in Biorefineries," John Wiley & Sons, USA (2013), pp. 608.

Ramey, D. and T.S. Yang, "Production of Butyric Acid and Butanol from Biomass," U. S. Department of Energy, Morgantown., 4 (2004).

Ranjbar, Z., M. Tajallipour, H.C. Niu and A. Dalai, "Water Removal from Ethanol Vapor by Adsorption on Canola Meal after Protein Extraction," Ind. Eng. Chem. Res. **52**, 14429-14440 (2013).

Raveendran, K., A. Ganesh and K.C. Khilar, "Pyrolysis characteristics of biomass and biomass components," Fuel. **75**, 987-998 (1996).

Rivera, F.A., G. Rodriguez and J.P. Bejarano, "Optimization of Ethanol Dehydration by PSA with 3A Zeolites," 13 AIChE Annual Meeting. **327c** (2013).

Ruthven, M., Douglas, "Principles of Adsorption and Adsorption Processes," John Wiley & Sons, US (1984), pp. 433.

Satterfield, C., "Heterogeneous Catalysis in Industrial Practice," McGraw-Hill Company (1980), pp. 416.

Shah, R.Y. and J.S. Dhrubo, "Bioalcohol as green energy- A review," Int. J. Cur. Sci. Res. **2**, 57-62 (2011).

Shahbeig, H., N. Bagheri, S.A. Ghorbanian, A. Hallajisani and S. Poorkarimi, "A new adsorption isotherm model of aqueous solutions on granular activated carbon," World. J. Model. Simulat. **9**, 243-254 (2013).

Sharma, P., A. Verma, R.K. Sidhu and O.P. Pandey, "Process parameter selection for strontium ferrite sintered magnets using Taguchi L9 orthogonal design," J. Mater. Proc. Technol. **168**, 147-151 (2005).

Simo, M., "Pressure Swing Adsorption Process for Ethanol Dehydration," ProQuest, USA (2008), pp. 158.

Statistics Canada, "Production of principal field crops," **2014** (a).

Sun, J., W. Wang, P. Wan, L. Hao, X. Luo and H. Gao, "Characterization of a Compound Starch-based Adsorbent for Alcohol-Water Azeotrope Dehydration," Adsorpt. Sci. Technol. **31**, 829-844 (2013).

Sun, N., C. Okoye, H.C. Niu and H. Wang, "Adsorption of Water and Ethanol by Biomaterials," Int. J. Green. Energ. **4**, 623-634 (2007).

Tajallipour, M., C. Niu and A. Dalai, "Ethanol Dehydration in a Pressure Swing Adsorption Process Using Canola Meal," Energ. Fuel. **27**, 6655-6664 (2013).

Theivandran, G., M.S. Ibrahim and M. Murugan, "Fourier Transform Infrared (Ft-Ir) Spectroscopic Analysis of *Spirulina Fusiformis*," J. Med. Plant. Stud. **4**, 30-32 (2015).

Thomas, W.J. and B.D. Crittenden, "Adsorption Technology and Design," Butterworth-Heinemann, Chicago (1998), pp. 271-129.

Thompson, R.K., J.J. McKinnon, A.F. Mustafa, D.D. Maenz, V.J. Racz and D.A. Christensen, "Chemical composition, ruminal kinetic parameters, and nutrient digestibility of ammonia treated oat hulls," Can. J. Anim. Sci. **82**, 103-109 (2002).

Thompson, A.B., S.J. Cope, T.D. Swift and J.M. Notestein, "Adsorption of n-butanol from dilute aqueous solution with grafted calixarenes," Langmuir. **27**, 11990-11998 (2011).

University of California Television (UCTV) and Berkeley Lab, "Hope or Hype? What's next for Biofuels?" Science at the Theatre. (2009).

USDA, F.A.S., "World Agricultural Supply and Demand Estimates," **WASDE-548**, 23-27 (2015).

USDA, F.A.S., "World Oats Production, Consumption, and Stocks," U. S. Department of Agriculture., 1 (2014).

Vareli, G., P.G. Demertzis and Akrida- Demertzi.K, "Effect of Regeneration Thermal Treatment of Cellulosic and Starchy Materials On Their Capacity to Separate Water and Ethanol," J. Cereal. Sci. **31**, 147-154 (2000).

Vareli, G.D., P.G. Demertzis and K. Akrida-Demertzi, "Effect of adsorbent particle size on the water-ethanol separation by cellulosic substrates," Dev. Food. Sci. **207**, 122-127 (1998).

Visioli, J.L., H. Enzweiler, C.R. Kuhn, M. Schwaab and A.M. Mazutti, "Recent advances on biobutanol production," Sust. Chem. Process. **2**, 1-9 (2014).

Westgate, J.P. and R.M. Ladisch, "Sorption of Organics and Water on Starch," Ind. Eng. Chem. Res. **32**, 1676-1680 (1993).

Witono, J.R., I.W. Noordergraaf, H.J. Heeres and L.P.B.M. Janssen, "Water absorption, retention and the swelling characteristics of cassava starch grafted with polyacrylic acid," Carbohyd. Polym. **103**, 325-332 (2014).

Wu, P., H. Gao, J.S. Sun, T. Ma, Y. Liu and F. Wang, "Biosorptive dehydration of tert-butyl alcohol using a starch-based adsorbent: Characterization and thermodynamics," Bioresour. Technol. **107**, 437-443 (2012).

Xu, F., J. Yu, T. Tesso, F. Dowell and D. Wang, "Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review," Appl. Energ. **104**, 801-809 (2013).

Yang, K., L. Zhu and B. Xing, "Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials," Environ. Sci. Technol. **10**, 1855-1861 (2006).

Yang, X., G. Tsai and G. Tsao, "Enhancement of in situ adsorption on the acetone-butanol fermentation by *Clostridium acetobutylicum*," Sep. Technol. **4**, 81-92 (1994).

Youngmi, K., R. Hendrickson, N. Mosier, A. Hilaly and R.M. Ladisch, "Cassava Starch Pearls as a Dessicant for Drying Ethanol," Ind. Eng. Chem. Res. **50**, 8678-8685 (2011).

Zayas, F.J., "Water Holding Capacity of Proteins," in "Functionality of Proteins in Food," Anonymous Springer Berlin Heidelberg, Germany (1997), pp. 76.